

JOURNAL
OF THE
PHYSICAL SOCIETY
OF JAPAN

Volume 15

1960

PT-1

Published by the
PHYSICAL SOCIETY OF JAPAN

JOURNAL

OF THE

PHYSICAL SOCIETY

OF JAPAN

Digitized by the Internet Archive
in 2024

Radiations from Ba¹⁴¹

By Kunio NAGATANI

*Department of Physics,
Tohoku University, Sendai*

Beta- and gamma-rays from 18-min Ba¹⁴¹ were investigated using scintillation spectrometers. Ba¹⁴¹ was made from photofission of natural uranium. The end-point energy of the beta-ray was determined to be 2.8-MeV and the gamma-rays of energies 0.125, 0.19, 0.28, 0.37, 0.46 and 0.61-MeV, respectively, were observed.

§ 1. Introduction

Barium isotopes are often used for monitoring fission yields. Radiochemical methods for separating barium from other fission products, therefore, are very well established.

In the course of radiochemical studies using a betatron, we have produced 18-min Ba¹⁴¹ which probably is an easier standard for shorter half-life studies than 85-min Ba¹³⁹ or 12.8-day Ba¹⁴⁰ which are usually employed as standards.

Not very much, however, was known about the radiations from 18-min Ba¹⁴¹.

Until very recent year measurements were only done by absorption method.^{1),2)} So, it is felt worth while to measure the radiations from this nuclide with scintillation spectrometers.

During the course of this investigation, results of such scintillation spectrometer studies were reported. These results are generally in good agreements with ours, but in the present experiment a few more gamma-rays were observed.

§ 2. Experimental Procedures and Results

For producing Ba¹⁴¹ from photofission, samples of UO₂Cl₂·HCl·2H₂O were irradiated for 20-min with bremsstrahlung from a 25-MeV betatron at Tohoku University.

For separating barium from other fission products of uranium a procedure described by Glendenin⁴⁾ was modified so that more rapid preparation of the source could be achieved.

After dissolving the irradiated uranium by fuming HNO₃, the barium was separated chemically with Na₂CrO₄ as precipitate of BaCrO₄. Before this step, the contaminations of other fission products were scavenged several times by Fe-carrier as precipitate of

Fe(OH)₃. This process could be performed within 10 minutes or so after the irradiation was finished.

The purities of these samples were checked by following the decay of the beta-rays. From the decay curve, 18-min component was obtained after subtracting out some long components. These long components were 85-min Ba¹³⁹ and 3.7-hr La¹⁴¹ which was the daughter product of 18-min Ba¹⁴¹. In this experiment the 11-min Ba¹⁴² was not separated since it took rather long time to do chemical separation. The decay curve is shown in Fig. 1.

Also, we detected the well known gamma-rays belonging to 12.8-day Ba¹⁴⁰ which was prepared by the same chemical procedures from the same uranium compound irradiated

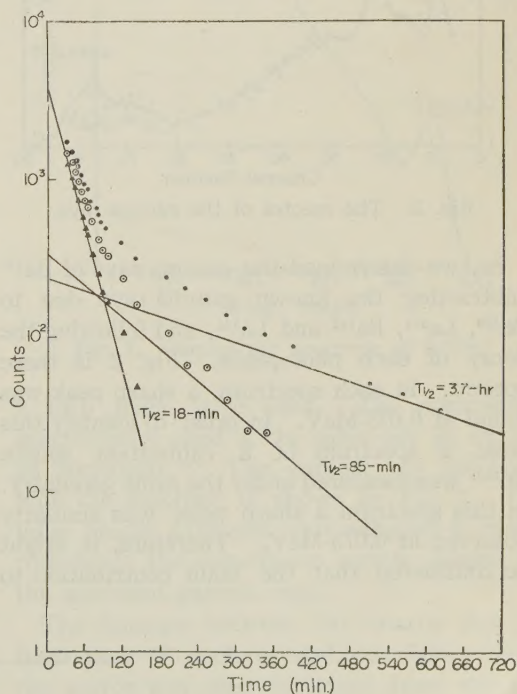


Fig. 1. The decay curve of the beta-rays.

in Japan Atomic Energy Research Reactor. No other gamma-rays than those of Ba^{140} were found in the source.

Consequently, it was considered that the samples contained only barium and the contaminations could be neglected. The gamma-rays were detected by a $1\frac{1}{2}'' \times 1\frac{1}{2}''$ NaI(Tl) crystal and a 100 channel pulse height analyzer. The spectra were very complicated because of short lived component which might be considered to be 11-min Ba^{142} and of its daughter product, 91-min La^{142} , in addition to the longer three components.

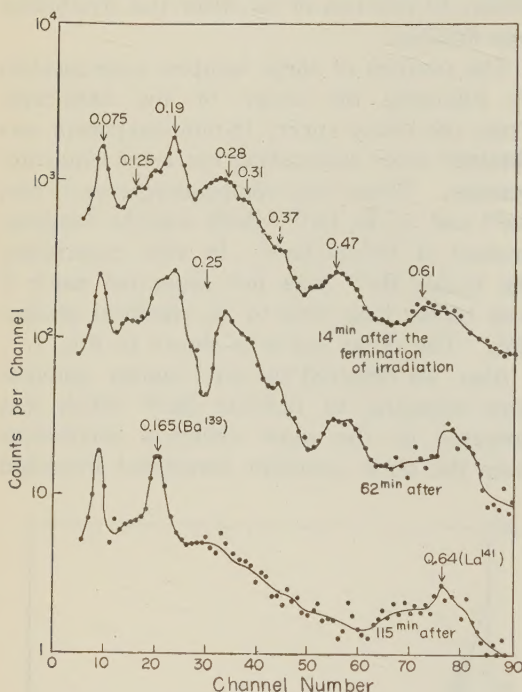


Fig. 2. The spectra of the gamma-rays.

So, we determined the gamma-rays of Ba^{141} subtracting the known gamma-rays due to Ba^{139} , La^{141} , Ba^{142} and La^{141} , and following the decay of each photopeaks. Fig. 2 is these spectra. In each spectrum, a sharp peak was found at 0.075-MeV. In order to identify this peak, a spectrum of a calibration source In^{114m} was measured under the same geometry. In this spectrum a sharp peak was similarly observed at 0.075-MeV. Therefore, it might be considered that the main contribution to

this peak came from a back scattering and a X-ray of lead blocks which were used for shielding. So, even if a gamma-ray of Ba^{141} was included in this peak, it was not to be so strong.

There was a very rapid decay at 0.25-MeV, it might be assigned to Ba^{142} .

In the previous investigation,³⁾ the gamma-rays were reported at energies 0.20, 0.29 and 0.46-MeV, respectively. In the present results, however, they were observed at energies 0.19, 0.28 and 0.46-MeV. Besides then, weak gamma-rays were also observed, at energies 0.125, 0.37 and 0.61-MeV. Also, around 0.31-MeV, a broad peak which might be considered to belong to Ba^{141} , was observed.

Table I. Gamma-rays of Ba^{141} .

Energy in MeV	Intensity ratios
0.125	25
0.19	100
0.28	45
0.37	40
0.46	20
0.61	15
0.31(?)	—

The intensity ratios were obtained from the photopeak areas in the spectra. The errors of these were several ten percent. The results are shown in Table I. The beta-rays were observed with an anthracene crystal and the end-point energy was determined to be 2.8-MeV. This is in agreement with the previous measurement.²⁾

Acknowledgement

The author wishes to thank Prof. H. Morinaga for his guidance through the course of this work.

References

- 1) A. Goldstein: NNES-PPR **9** 1096 (1951).
- 2) H. A. Levy and B. Zemel: reported in Oak Ridge National Laboratory Report ORNL-176 Nov. (1948) (unpublished).
- 3) R. P. Schuman, E. H. Turk, R. L. Heathm: Bull. Amer. Phys. Soc. **3**, no. 5, 315.
- 4) L. E. Glendenin: NNES-PPR **9** 1460.

Angular Correlation Measurements in the Decay of $\text{In}^{114\text{m}}$

By Mitsuhiro KAWAMURA

Department of Physics, Kyoto Prefectural University, Kyoto

(Received August 22, 1959)

The directional correlation and the polarization-direction correlation of the 722 Kev-556 Kev gamma-gamma cascade in Cd^{114} have been measured. It is found that the decay sequence of this cascade agrees well with the $4(E2)2(E2)0$ sequence. The ratio of the rate of the positron decay to that of the cascade decay is also obtained as 3×10^{-3} .

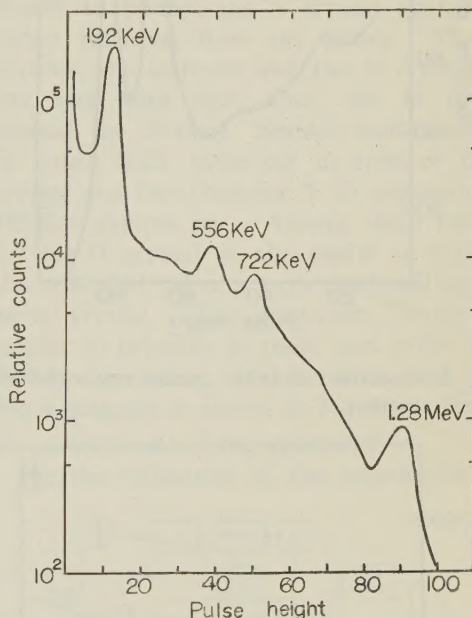
§ 1. Introduction

The 50-day isomeric state of $\text{In}^{114\text{m}}$ decays to Sn^{114} by electron emission through the ground state of In^{114} and to Cd^{114} by electron capture. In the latter transition, it is well confirmed from the coincidence measurements¹⁾⁻⁷⁾ and the Coulomb excitation experiments⁸⁾⁻¹⁰⁾ that the 556 Kev gamma ray is emitted in succession to the 722 Kev gamma ray. For this gamma ray cascade, many directional correlation measurements were carried out and their results were found to fit well with the theoretical correlation function in either case of the spin assignment of 4 or 2 to the 1.28 Mev level. Now, in view of the fact that the energy ratio of the first two excited states in this nucleus is nearly two, the excitation should have the vibrational character.¹¹⁾ Recently, a 2^+ level having the energy of 1.20 Mev was found through the experiments of the Coulomb excitation¹²⁾ and the (n, γ) reaction.¹³⁾ Combining this with the spin assignment of 4 to the 1.28 Mev level, the existence of the triplet of levels as described by Scharf-Goldhaber and Weneser¹⁴⁾ can be suggested. Therefore, it is worth while to determine decisively the spin and the parity of the 1.28 Mev level.

§ 2. Directional Correlation Experiments

The source material obtained from Oak Ridge National Laboratory was InCl_3 in HCl solution. The gamma ray spectrum of $\text{In}^{114\text{m}}$ decay was measured by using an NaI(Tl) crystal of the well type which had $1\frac{1}{2}$ inch in diameter and 2 inch thick having a hole of $\frac{3}{8}$ inch in diameter and $1\frac{1}{2}$ inch in depth drilled along the center axis. The result is shown in Fig. 1. A higher peak seen in the figure corresponds mainly to the sum peak of the 556 Kev and 722 Kev gamma rays. In

measuring the directional correlation, the 192 Kev gamma ray having strong intensity was suppressed by using lead absorbers of 5 mm thick placed on the front face of both detectors. Through this experiment, the RCA 5819 photomultiplier tubes mounted with NaI(Tl) crystals of $1\frac{1}{2}$ inch in diameter and

Fig. 1. Gamma ray spectrum of $\text{In}^{114\text{m}}$.

1 inch thick were used. The coincidence spectrometer used is the same one as reported previously.¹⁵⁾ The gamma ray spectrum with the absorber is shown in Fig. 2. The pulse height analyzers were adjusted to reject completely the coincidence counts caused by the scattered gamma rays.

The distance between the source and the front face of each crystal was 7 cm. Since the source was used in liquid form and the measured life-time of the intermediate state

was shorter than 2.3×10^{-10} sec,^{16),17)} the attenuation of the anisotropy by the extranuclear effect was expected to be mostly avoided. The experimental result thus obtained is shown in Fig. 3. Some anomaly found at the angles of 165° and 180° can be explained as the effect of the annihilation gamma rays created at the source position. This viewpoint was confirmed further by another directional correlation experiment in which one pulse height analyzer was adjusted to count only the gamma ray higher than 640 Kev so that any coincidence counts of the annihilation gamma ray should be completely excluded.

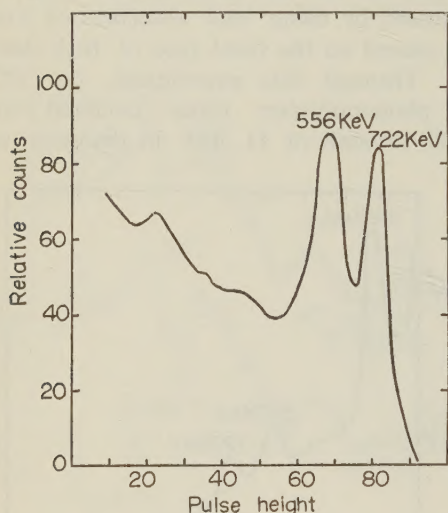


Fig. 2. Spectrum of $\text{In}^{114\text{m}}$ gamma ray with 5mm lead absorber.

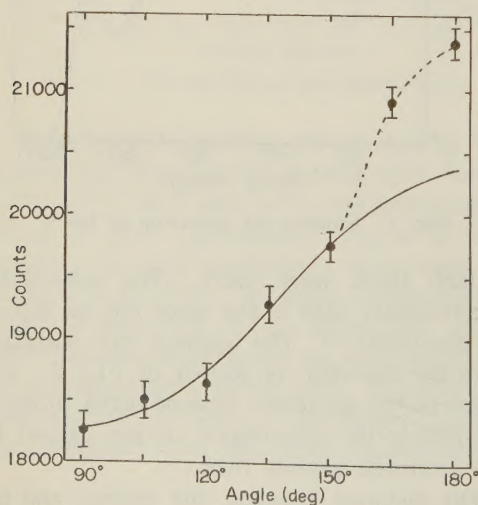


Fig. 3. Directional correlation of the 556KeV-722KeV gamma rays including the contribution of the annihilation radiations.

ed. The result is shown in Fig. 4. The disappearance of the above-mentioned anomaly confirms the existence of the annihilation gamma rays due to the positron decay. Moreover, by using the experimental data given in Fig. 3, the ratio of the rate of the positron decay to that of the cascade decay could be estimated as 3×10^{-3} . Thus, if the branching fraction for the K-capture decay to the 1.28 Mev level of Cd^{114} per decay of $\text{In}^{114\text{m}}$ is 3.5% as reported by John *et al.*⁶⁾, that for the positron decay becomes 0.01%.

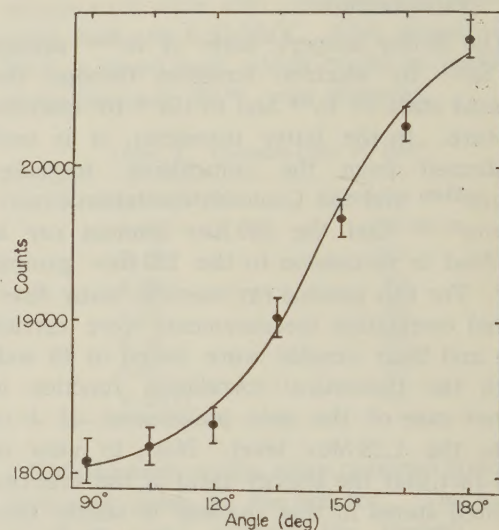


Fig. 4. Directional correlation of the 556KeV-722KeV gamma rays not including the contribution of the annihilation radiations.

The result shown in Fig. 4 can be expressed as

$$W(\theta) = 1 + (0.091 \pm 0.006)P_2(\cos \theta) + (0.030 \pm 0.009)P_4(\cos \theta). \quad (1)$$

This formula is corrected for the finite angular resolution. The theoretical values of A_2 and A_4 for various combinations of the spin assignments to the second excited state and the multipole mixings for the 722 Kev gamma ray are tabulated in Table I with the experimental values. The fit between the experimental and theoretical values is tolerably well in either case of the $4(Q)2(Q)0$ or $2(D, Q)2(Q)0$ ($\delta = -0.20$) sequence. Therefore, it is difficult to choose the best case from the result of the directional correlation measurement. But this ambiguity can be removed by the polarization-direction correlation measurement.

Table I. The theoretical values of A_2 and A_4 for various combinations of the spin assignments to the 2nd excited state and the multipole mixings for the 722Kev gamma ray and the experimental values.

Cascade	A_2	A_4	δ^*
4(Q)2(Q)0	0.1020	0.0091	
3(D, Q)2(Q)0	0.1330	-0.0067	-0.30
3(D, Q)2(Q)0	0.1064	-0.0049	-0.25
3(D, Q)2(Q)0	0.0740	-0.0031	-0.20
2(D, Q)2(Q)0	0.0564	0.0196	-0.25
2(D, Q)2(Q)0	0.0967	0.0126	-0.20
2(D, Q)2(Q)0	0.1357	0.0072	-0.15
Experimental	0.091 ± 0.006	0.030 ± 0.009	

* δ is the ratio of the reduced matrix element of the quadrupole transition to that of the dipole transition.

§ 3. Polarization-Direction Correlation

a) Polarimeter

Schematic arrangement of the polarimeter is shown in Fig. 5. In this figure, the Z-axis is perpendicular to the plane containing the center-axis of the scatterer (X-axis) and that of the direction counter, and the Y-axis is parallel to the center-axis of the direction counter.

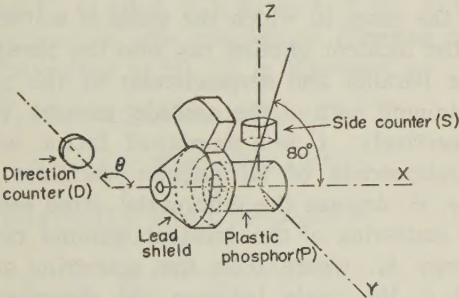


Fig. 5. Schematic arrangement of the polarimeter.

A plastic phosphor (P) composed of polystyrene, *p*-terphenyl (1%), POPOP (0.03%) and zincstearate (0.03%) was used as the scatterer and the crystals for the direction counter (D) and the side counter (S) were NaI(Tl) of 1½ inch in diameter and 1 inch thick. The distances between the source and the front face of the D crystal and that of the phosphor P are both 5 cm. The front face of the S crystal is placed at a distance of 5 cm from the X-axis, and the line connecting the center of the phosphor P and that of the front face of the S crystal makes an angle of 80° with the X-axis. This angle gives the maximum asymmetry ratio¹⁸⁾ for the gamma

ray of about 750 Kev. The gamma ray beam collimated into the phosphor P is scattered in the same phosphor and detected by the S crystal. The lead shield of 5 cm thick is sufficient to protect the S crystal against the direct radiation from the source. The collimator, the scatterer and the S crystal, being fixed with each other, can be rotated around the X-axis. Besides, lead absorbers of 5 mm thick were put in front of the D crystal and the phosphor P to attenuate the 192 Kev gamma ray. Among them the one for the D crystal is also useful to suppress the scattered gamma rays entering into the same crystal. The electronic circuits are similar in principle to those used in the directional correlation measurements and their block diagram is shown in Fig. 6.

b) Adjustment of the apparatus

For the calibration of the polarimeter, the

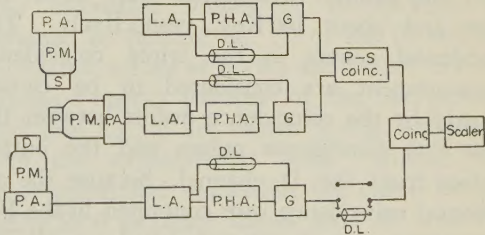


Fig. 6. Block diagram of the triple coincidence circuits used for the measurement of the polarization-direction correlation.

- P.M.—RCA5819; P.A.—6AK5 cathode follower
- L.A.—Model 500 linear amplifier
- P.H.A.—pulse height analyzer
- G—gate circuit; Coinc—double coincidence circuit
- D.L.—G.E. DL1100 giving 0.5μ sec delay.

660 Kev gamma ray of Cs^{137} was used, because the gamma ray energy of this isotope was nearly equal to that of $\text{In}^{114\text{m}}$. The spectrum of the pulses in the S channel which are in coincidence with all pulses in the P channel is shown in Fig. 7. In this figure,

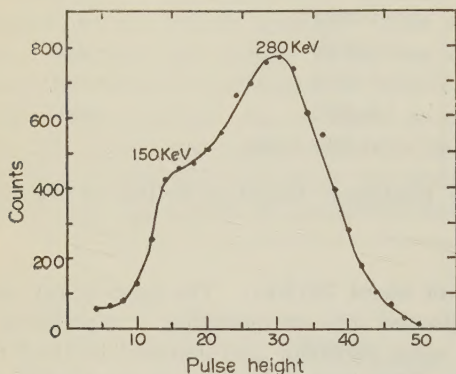


Fig. 7. Gamma ray spectrum of the S-channel in coincidence with all pulses in P-channel.

the higher peak, in view of its energy, corresponds to singly scattered gamma rays from the phosphor P and the swelling seen at about 150 Kev can be explained to be caused by doubly scattered gamma rays, because the pulses of this part are in coincidence mainly with those of the low energy part of the P channel spectrum. Undesirable admixture of doubly scattered component mentioned above was avoided by adjusting the pulse height analyzer in the S channel to stop out the pulses corresponding to the energy less than 220 Kev. The pulse height analyzers in the D and P channel were adjusted so as to count only the gamma rays higher than about 120 Kev and about 100 Kev, respectively. The accidental counts in the triple coincidence measurement are considered to be caused mostly by the coincidence events between the true P-S coincidence pulses and the output pulses from the D channel, because the accidental coincidence rate contained in the P-S coincidence rate is estimated to be negligible in comparison with the true coincidence rate due to small single counts in the side counter. These counts were measured by delaying the pulses in the D channel by $0.5 \mu\text{sec}$ and the true triple coincidence counts amounted to about 10/min throughout this experiment. The source position was adjusted so that the P-S coincidence rate should be equal to each

other for the perpendicular and parallel positions.*

c) Asymmetry parameter of the polarimeter

The correlation function expected for the polarization-direction correlation measurements on cascade gamma rays has been calculated by several authors.^{19), 20)} The calculated correlation is given as a function of θ and φ , where θ is the angle between the directions of emissions of the cascade gamma rays and φ is the angle between the electric vector of the gamma ray entering into the phosphor P and the normal to the plane of the two gamma rays. When the polarization-direction correlation function for a cascade is given by $W(\theta, \varphi)$ and only the electric vectors for $\varphi = 90^\circ$ and 0° are measured, the triple coincidence rate $N_{||}(\theta)$ and $N_{\perp}(\theta)$ can be written²¹⁾ as

$$\begin{aligned} N_{||}(\theta) &= C [W(\theta, 90^\circ) d\sigma(\vartheta, 0^\circ) \\ &\quad + W(\theta, 0^\circ) d\sigma(\vartheta, 90^\circ)], \\ N_{\perp}(\theta) &= C [W(\theta, 90^\circ) d\sigma(\vartheta, 90^\circ) \\ &\quad + W(\theta, 0^\circ) d\sigma(\vartheta, 0^\circ)]. \end{aligned} \quad (2)$$

Here, $N_{||}(\theta)$ and $N_{\perp}(\theta)$ represent the rates for the cases in which the plane of scattering of the incident gamma ray into the phosphor P is parallel and perpendicular to the plane containing both of the cascade gamma rays, respectively. C is a numerical factor which is independent of all angular variables and $d\sigma(\vartheta, \psi)$ denotes the differential cross section for scattering of the incident gamma ray of energy k_0 , where ϑ is the scattering angle and ψ the angle between the direction of polarization of the incident gamma ray and the plane of scattering. $d\sigma(\vartheta, \psi)$ is given by the well-known Klein-Nishina formula²²⁾ as:

$$\begin{aligned} d\sigma(\vartheta, \psi) &= \frac{e^4}{2m^2c^4} \frac{k^2}{k_0^2} \left[\frac{k}{k_0} + \frac{k_0}{k} \right. \\ &\quad \left. - 2 \sin^2 \vartheta \cos \psi \right] d\Omega, \end{aligned} \quad (3)$$

with

$$k = \frac{k_0}{1 + (k_0/mc^2)(1 - \cos \vartheta)}, \quad (4)$$

where k is the energy of the secondary quantum.

* The perpendicular and parallel positions correspond to the positions at which the axis of the S crystal coincides with the Z-axis and the Y-axis, respectively.

In estimating $N_{11}(\theta)$ and $N_{\perp}(\theta)$ theoretically, the effects of finite size of all the detectors were not sufficiently taken into account in Metzger and Deutsch's paper.¹⁸⁾

This situation is improved in the present paper. However, straight-forward calculation is so complicated and tedious that some simplifications have been introduced in the actual calculation. Firstly, the D crystal is substituted as shown in Fig. 8 by five points D_i ($i=0, 1, 2, 3, 4$), all of which lie on a plane at

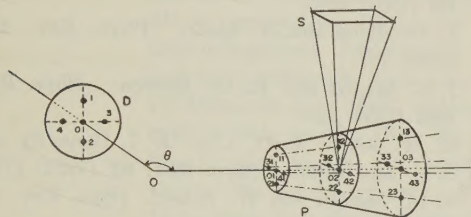


Fig. 8. Illustrative figure of the scattering phosphor, the direction and the side crystals.

the middle of the front and back faces of the crystal. Similarly, the phosphor P is represented, as seen in the same figure, by fifteen points P_{jk} ($j=0, 1, 2, 3, 4; k=1, 2, 3$). In this approximation, the coincidence counting rate corresponding to Eq. (2) is expressed as

$$\begin{aligned}\bar{N}_{11}(\theta) &= A \left[\sum_{ij} W(\theta_{ij}, 90^\circ) \sigma_{ij}(0^\circ) \right. \\ &\quad \left. + \sum_{ij} W(\theta_{ij}, 0^\circ) \sigma_{ij}(90^\circ) \right], \\ \bar{N}_{\perp}(\theta) &= A \left[\sum_{ij} W(\theta_{ij}, 90^\circ) \sigma_{ij}(90^\circ) \right. \\ &\quad \left. + \sum_{ij} W(\theta_{ij}, 0^\circ) \sigma_{ij}(0^\circ) \right],\end{aligned}\quad (5)$$

where A is a numerical factor which is independent of all angular variables and θ_{ij} is the angle between $\overrightarrow{OD_i}$ and $\overrightarrow{OP_{jk}}$.

$\sigma_{ij}(\chi)$ ($\chi=0^\circ$ or 90°) is expressed as

$$\sigma_{ij}(\chi) = \sum_k e^{-\mu x_{jk}} d\sigma_{ijk}(\chi). \quad (6)$$

In this formula, μ is the linear absorption coefficient of the plastic phosphor for the incident gamma ray, and x_{jk} is the distance between P_{j1} and P_{jk} . $d\sigma_{ijk}(0^\circ)$ denotes the cross section that the incident gamma ray polarized linearly along the normal to the $(\overrightarrow{OD_i}, \overrightarrow{OP_{jk}})$ plane is scattered at the point P_{jk} and enters into the S crystal at the perpendicular position. $d\sigma_{ijk}(90^\circ)$ corresponds to the one for the parallel position. To simplify the calculation, the S crystal is replaced by a square, as shown in Fig. 8, which lies on a

plane placed at the middle of the front and back faces of crystal and has the same area as that of a circle of 1.1/2 inch in diameter. $\sigma_{ij}(0^\circ)$ and $\sigma_{ij}(90^\circ)$ depend on the geometry of the polarimeter and the energy of the incident gamma ray and are called asymmetry parameters of the polarimeter. The result of numerical calculation on this parameter is given for various gamma ray energies in reference 23). For the 0.89 Mev–1.12 Mev gamma-gamma cascade of Sc^{46} which has the well-established decay sequence of $4(E2)2(E2)0$, the calculated value of $\bar{N}_{11}(90^\circ)/\bar{N}_{\perp}(90^\circ)$ was 0.89, while the experimental one was obtained as 0.92 ± 0.03 . The fit seems to be well within the limit of standard error.

d) Measurement and result

Since the measured two gamma rays of Cd^{114} have nearly the same energy, the efficiency of the polarimeter counting one gamma ray by the phosphor P and the other by the D crystal is approximately equal to that of the reversed case. Taking this condition into consideration, the averaged polarization-direction correlation function can be expressed as follows. Namely, for $4(E2) \cdot 2(E2)0$,

$$\begin{aligned}\langle W(\theta, \varphi) \rangle_{av} &= 1 + 0.1020 P_2(\cos \theta) \\ &\quad + 0.0091 P_4(\cos \theta) + [-0.0510 P_2^2(\cos \theta) \\ &\quad + 0.0008 P_4^2(\cos \theta)] \cos 2\varphi,\end{aligned}\quad (7)$$

and for $2(E2+M1)2(E2)0$, where $\delta = -0.20$,

$$\begin{aligned}\langle W(\theta, \varphi) \rangle_{av} &= 1 + 0.0967 P_2(\cos \theta) \\ &\quad + 0.0126 P_4(\cos \theta) + [-0.0953 P_2^2(\cos \theta) \\ &\quad + 0.0011 P_4^2(\cos \theta)] \cos 2\varphi.\end{aligned}\quad (8)$$

The calculated values of $\bar{N}_{11}(\theta)/\bar{N}_{\perp}(\theta)$ as obtained by putting Eq. (7) or Eq. (8) and the calculated values of $\sigma_{ij}(0^\circ)$ and $\sigma_{ij}(90^\circ)$ for the averaged energy 640 Kev of the two gamma rays into Eq. (5) are shown in Fig. 9 together with the experimental ones. Among the above-mentioned sequences, the curve for the $4(E2)2(E2)0$ sequence shows good fit with the measured values.

§ 4. Discussion

As seen in Table I, A_2 and A_4 from the measured correlation function show some disagreement with those of the $4(E2)2(E2)0$ sequence. This disagreement can be removed by taking the contribution of the gamma ray from the recently found 2^+ level,^{12), 13)} which

is situated by 0.08 Mev below the 1.28 Mev level, into consideration in addition to that of the $4(E2)2(E2)0$ sequence. Namely, good fit with the experimental A_2 and A_4 could be obtained by putting $\delta = +78.2$ for the gamma ray emitted in the transition from the 2^+ level to the first excited state and by estimating the rate of this transition being 7% to that from the 4^+ level. The estimated intensity of 7% is consistent with the one obtained from the theoretical estimation of the K-electron capture transition²⁴⁾ from the ground state of In^{114} to the 1.20 Mev level.

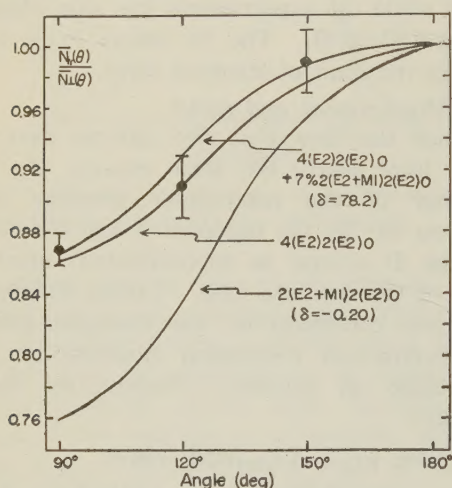


Fig. 9. Comparison between the experimental and theoretical polarization-direction correlations.

After this correction, the theoretical polarization-direction correlation function becomes

$$\begin{aligned} \langle W(\theta, \varphi) \rangle_{av} = & 1 + 0.091 P_2(\cos \theta) \\ & + 0.030 P_4(\cos \theta) + [-0.045 P_2^2(\cos \theta) \\ & + 0.003 P_4^2(\cos \theta)] \cos 2\varphi. \end{aligned} \quad (9)$$

The value of the $\bar{N}_1(\theta)/\bar{N}_4(\theta)$ calculated from this function fits well with the experimental one as shown in Fig. 9.

Acknowledgements

The author wishes to express his gratitude to Prof. K. Kimura of Kyoto University and Prof. T. Hayashi for their encouragements and discussions throughout this work. He is also deeply indebted to his colleague Mr. A. Aoki who has been in cooperation during the whole experiments. He also expresses his sincere thanks to Messrs. Y. Ishizaki, M. Oda and

I. Miura, Institute for Nuclear Study, University of Tokyo, for giving many valuable informations on the plastic phosphor. This work was partly supported by a grant-in-aid for scientific research of the Ministry of Education.

References

- 1) R. M. Steffen and J. N. Brazos: Phys. Rev. **99** (1955) 1646.
- 2) J. N. Brazos and R. M. Steffen: Phys. Rev. **99** (1955) 1645.
- 3) L. Grodzins and H. Motz: Phys. Rev. **102** (1956) 761.
- 4) J. N. Brazos and R. M. Steffen: Phys. Rev. **102** (1956) 753.
- 5) M. W. Johns, C. D. Cox, R. J. Donnelly and C. C. McMullen: Phys. Rev. **87** (1952) 1134.
- 6) R. M. Steffen and W. Zobel: Phys. Rev. **88** (1952) 170.
- 7) E. D. Klema and F. K. McGowan: Phys. Rev. **87** (1952) 524.
- 8) G. M. Temmer and N. P. Heydenberg: Phys. Rev. **104** (1956) 967.
- 9) P. H. Stelson and F. K. McGowan: Phys. Rev. **110** (1958) 489.
- 10) F. K. McGowan and P. H. Stelson: Phys. Rev. **106** (1957) 552.
- 11) A. Bohr and B. R. Mottelson: K. Dansk. Vidensk. Selsk. Mat-fys. Medd. **27** no. 16 (1953).
- 12) P. H. Stelson and F. K. McGowan: Bull. Amer. Phys. Soc. Ser. **2** (1957) 267.
- 13) H. T. Motz: Phys. Rev. **104** (1956) 1353.
- 14) G. Scharf-Goldhaber and J. Weneser: Phys. Rev. **98** (1955) 212.
- 15) T. Hayashi: J. Phys. Soc. Japan **13** (1958) 117.
- 16) S. C. Daubin and D. R. Hamilton: Phys. Rev. **99** (1955) 683.
- 17) G. M. Temmer and N. P. Heydenberg: Phys. Rev. **98** (1955) 1308.
- 18) F. Metzger and M. Deutsch: Phys. Rev. **78** (1950) 551.
- 19) D. R. Hamilton: Phys. Rev. **74** (1948) 782.
- 20) L. C. Biedenharn and M. E. Rose: Rev. Mod. Phys. **25** (1953) 729.
- 21) G. R. Bishop and J. P. Perez Y. Jorba: Phys. Rev. **98** (1955) 89.
- 22) W. Heitler: *The Quantum Theory of Radiation*, 3rd ed. (Oxford Univ. Press, 1954) 217.
- 23) M. Kawamura, A. Aoki and T. Hayashi: Soc. Rep. Kyoto Pref. Univ. **3** (1959) A5.
- 24) M. E. Rose: *Beta and Gamma Ray Spectroscopy* edited by Kai Siegbahn (North Holland Publishing Company, Amsterdam, 1955) Chap. IX p. 273.

Elastic Scattering of 14 MeV Protons by Deuterons and by Protons

By Seishi KIKUCHI, Junpei SANADA, Shigeki SUWA, Izuo HAYASHI,
Keigo NISIMURA and Kiyoji FUKUNAGA*

*Institute for Nuclear Study, University of Tokyo,
Tanashi-Machi, Tokyo*

(Received September 2, 1959)

The differential cross sections for the elastic scattering of 13.93 MeV protons by deuterons were measured with accuracy varying from 1 to 3% at angles from 12° to 164° in the center-of-mass system. A shallow Coulomb-nuclear interference minimum near 17° was observed. The angular distribution is in good agreement with that of neutrons scattered by deuterons at 14 MeV, although the p - d cross sections seem systematically a little smaller than the n - d cross sections at backward angles. For forward angles, the experimental results contradict with the prediction of the existing theory. The small-angle p - d elastic scattering at 10.14 MeV was also investigated and a similar shallow Coulomb-nuclear interference was observed, in contrast with the theoretical curve of Christian and Gammel.

The p - p scattering experiment at 14.16 MeV is also described. Measurements were made with accuracy of 1 to 2% for angles from 30° to 114° in the center-of-mass system.

§ 1. Introduction

As one of the scattering experiments on light nuclei which we intend to investigate using the beam of the INSJ 160 cm variable energy cyclotron, the angular distribution of the elastically scattered protons by deuterons at 13.93 MeV was studied. The investigation of the break-up protons from the p - d interaction was made in parallel. This will be reported in another paper in the future.

The nucleon-deuteron system has been the subject of many experimental and theoretical investigations¹⁾, in the hope of finding some informations on the nuclear forces, e.g. the nature of n - n forces, evidence for charge symmetry, existence of three-body forces and so on. As for the p - d elastic scattering in the intermediate energy region above 10 MeV, two carefully measured data at 20.6 MeV²⁾ and at 40 MeV³⁾ have recently been published. But an accurate p - d experiment at 14 MeV seems most convenient for the comparison of p - d and n - d scattering, since the most precise experiments of the n - d elastic scattering in this energy region have already been performed at 14 MeV.⁴⁾

Christian and Gammel⁵⁾ analysed the p - d and n - d scattering data in the energy range of 1 to 14 MeV, obtaining good agreement with experiments. This seems to show, as they explained, that much information on the n - n forces can not be expected from the analysis of the elastic scattering experiment in this energy region. But as has been shown by de Borde and Massey⁶⁾, who also obtained with Serber-forces the angular distribution for the n - d elastic scattering at 14 MeV in reasonable agreement with experiments, there are still considerable discrepancies between theory and experiment for the p - d scattering at small angles in the energy region above 10 MeV. Seagrave and Cranberg have recently shown⁷⁾ that the experimental results at low energy, near 3 MeV, are also somewhat different from the expectation of the theory. A discrepancy seems to exist also at 9.7 MeV; while the angular distribution curve due to Christian and Gammel shows a marked Coulomb-nuclear interference minimum near 20° c.m., the experimental curve is rather flat and distinctively higher than the theoretical one at these small angles^{5), 8)}. Therefore, we investigated also the small-angle p - d scattering at 10 MeV with improved angular resolution.

* Department of Physics, Faculty of Science,
University of Kyoto, Kyoto

The proton-proton scattering experiment at 14 MeV was originally performed in order to check our experimental procedures in the p - d experiment. In spite of insufficient accuracies at small angles, we will report the results in view of the recent general interest in the p - p scattering at intermediate energies^{9),10)}. We intend to perform a more elaborate and accurate experiment at the same energy in the near future.

§2. Experimental Arrangements

The experimental arrangements were almost the same as those described in detail previously¹¹⁾. The characteristic features are repeated here briefly.

(i) Beam collimation

The external proton beam from the cyclotron is focused at the target position by means of a pair of quadrupole magnets and a sector-type bending magnet¹²⁾. The first defining slit 7 mm wide and the second defining hole of 3.5 mm diameter are located at 446 cm and at 54 cm from the center of the scattering chamber, respectively. Among several non-defining diaphragms, the final anti-scattering baffle of 6 mm diameter lying 35 cm beyond the second defining hole limits the spray of the protons off the last defining hole edge to a cone of half-angle 0.6° , so that the front slit of the detector sees no edge of the collimator hole even at a counter angle of 5° . All these diaphragms were made of graphite. That the actual main beam was even more parallel than defined by this collimator was confirmed by the beam spot 4 mm wide by 3.5 mm high on a lucite plate placed on the turn table in the scattering chamber.

(ii) Scattering chamber and gas target chamber

A 15 cm diameter gas target chamber¹¹⁾ with a 25 micron Mylar window, which was 1.6 cm high and extended to 290° of arc, was located at the center of the 100 cm diameter scattering chamber¹²⁾.

(iii) Detector system

Two detector systems were mounted on the turn table in the scattering chamber, one for smaller angles and the other for larger angles, lying 45° apart from each other. The defining slits were made of 0.6 mm thick brass. The dimensions of the slits are summarized in Table I.

Scattered protons and recoil deuterons were

Table I. Slit dimensions (in millimeters)

	Detector I	Detector II
Width of front slit	2.023	5.007
Width of rear slit	2.014	4.996
Height of rear slit	6.008	7.661
Distance from the scattering center to rear slit	304.2	262.2
Distance between slits	200.2	143.1

detected by the scintillation counters mounted behind the slits. For the detector I which was used for smaller angles, a 1.5 mm thick NaI crystal was used, while for the detector II, a CsI crystal as thin as 0.5 mm was used in order to reduce gamma-ray or neutron background. Thus, the p - d elastic proton peak in the pulse height spectrum could be well resolved from the background and the cross section could be measured at angles up to 110° in the laboratory system. Another scintillation detector set on the side wall of the scattering chamber at 40° laboratory angle was used as a monitor.

(iv) Control of the beam energy

Method of measurement of the beam energy was described previously¹¹⁾. With a carbon diaphragm 2 mm wide by 5 mm high inserted in the vacuum tank of the cyclotron and the collimator slits described in (i), the beam path was finely defined, and constancy of the beam energy was monitored by means of the proton resonance signal from the above-mentioned sector magnet. Thus, the beam energy was considered to be kept constant within 0.4% throughout the course of the experiment.

§3. The p - d Elastic Scattering at 13.93 MeV

(i) Procedures

Deuterium gas of 99% purity was obtained by electrolysis from heavy water and by passing through a heated palladium tube. The pressure of the target gas was 30 cm Hg.

Pulses from the detector I was recorded with two 20-channel pulse height analysers whose channels were set in series. Another 20-channel pulse height analyser was used to record the pulses from the detector II at the same time. A typical pulse height distribution is shown in Fig. 1.

The main peak was found to be always accompanied by a uniformly distributed low-pulse-height tail. Such a tail was more clear-

ly seen in the case of the $p-p$ scattering. In order to investigate the origin of the tail, a $p-p$ check run was performed, in which the coincidences between scattered and recoil protons were observed with a defining counter set at 45° on one side accompanied by a conjugate counter with appropriate aperture set at 45° on the other side. In coincidence counting, even with sufficiently low bias-settings,

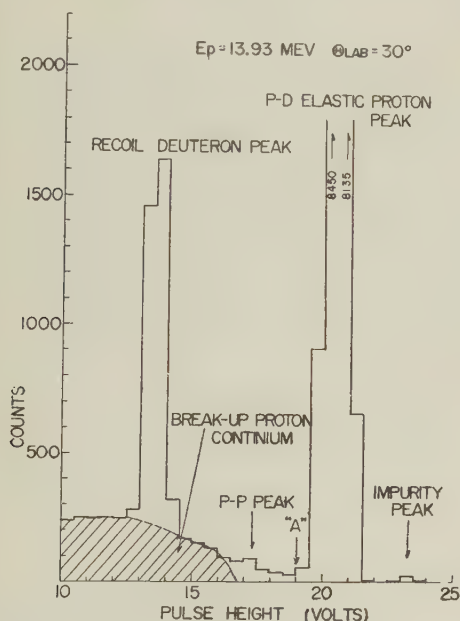


Fig. 1. Pulse height distribution of charged particles from the $p-d$ interaction at 13.93 MeV. The threshold channel for the elastic peak is indicated by "A".

the amount of the tail relative to the main peak was reduced to one-fifth of that in single counting. It can be concluded from this fact that the greater part of the tail is not due to the low energy component of the incident beam, but due to the multiple scattering by the detector slit-edges, mainly by its front slit-edges. The total number of counts in the tail remaining in the coincidence counting still amounted to 0.7% of those in the peak, but taking into account the geometry used, we can conclude that at least half of them are due to the slit-edge scattering. Therefore, in determining the number of the protons scattered by deuterons, we set the cutoff threshold just below the main peak and discarded all counts falling in the tail (Fig. 1).

The recoil-deuteron peak lies on or partly on the background arising from the break-up

protons. The method of subtracting this background is seen from Fig. 1. Correctness of this procedure was assured for some angles by the results of the $p-d$ break-up experiment, in which protons and deuterons were discriminated with a particle-selecting three-proportional counter combined with a scintillation counter¹³).

Two independent data-taking runs were performed and in each run the measurements at some angles were repeated at intervals throughout the run to detect any drift of the instruments and the increase in the impurities in the target gas. All the measurements for the same angle agreed with each other within the experimental error.

(ii) Results

The final results are presented in Table II. They are based on the weighted means of the individual data for each angle. The relativistic relations were used in transforming the angle and the cross section from the laboratory to the center-of-mass system. The energy of the proton beam used was 13.93 ± 0.07 MeV.

(iii) Corrections and errors

(a) Impurities in the target gas.

Hydrogen contamination in the target gas was found to increase with time because of evolution of impurity gases, probably H_2O and other organic compounds. The amount of the hydrogen atoms as a function of time could be measured within the accuracy of 20% by using the well-resolved $p-p$ peaks in the pulse height spectra at some angles larger than 21° (see Fig. 1) and the $p-p$ cross sections which will be described in Sec. 4. Thus, the initially contained hydrogen component was also determined to be $1.0 \pm 0.2\%$. Accuracy of this method of determination was confirmed by mass-spectroscopic analysis. Although impurities other than hydrogen were found to be negligible in the initial gas, the impurity peak due to the protons scattered by heavier nuclei began to appear and increased with time accompanied by the above mentioned increase in hydrogen contamination. At laboratory angles of 21° and smaller, the peaks due to the impurities of hydrogen and heavier nuclei could not be resolved from the $p-d$ elastic peak. The data at these angles must be corrected for these back-grounds. Corrections for the protons scattered by hydrogen

Table II. Differential cross sections for elastic scattering of 13.93 MeV protons by deuterons in the center-of-mass system
Angles denoted by (d) are recoil deuteron points

θ c.m. (degrees)	σ c.m. (mb/steradian)	Probable error %
11.70	134.4	4.8
13.20	120.7	2.4
14.70	117.5	1.9
16.20	112.8	1.7
17.70	114.0	1.5
19.20	113.4	1.4
20.69	113.5	1.3
22.18	115.2	1.1
23.68	114.8	1.2
25.16	112.7	1.2
26.65	114.0	1.2
28.14	113.1	1.1
29.62	112.5	1.1
31.10	112.1	1.1
34.06	109.1	1.0
37.00	103.8	1.0
40.66	97.6	1.1
44.30	92.3	1.0
51.51	81.9	1.1
58.61	70.5	1.1
65.59	60.1	1.1
72.42	50.3	1.1
79.10	41.6	1.3
80.55	39.9	1.1
81.85	37.6	1.2
83.15	36.3	1.1
84.52	35.0	1.1
85.58	33.5	1.3
85.73	33.7	1.1
87.00	32.2	1.1
88.27	30.7	1.1
89.52	29.5	1.1
90.34(d)	28.3	1.7
90.78	28.6	1.0
91.88	27.6	1.4
92.02	27.2	1.0
93.25	26.3	1.0
95.80	24.1	1.0
98.10	21.8	1.0
100.35(d)	20.3	1.7
103.95	17.0	0.9
109.58	13.3	1.3
110.35(d)	13.2	2.4
114.96	10.79	1.1
120.08	9.03	1.4
120.36(d)	9.02	3.4
124.96	8.41	1.4
125.36(d)	8.45	3.4
129.57	9.61	1.3
130.37(d)	9.54	2.7
133.95	12.22	1.3
134.37(d)	11.76	2.8
138.08	16.1	1.3
138.38(d)	16.6	3.1
140.38(d)	19.5	2.7
142.38(d)	22.8	2.6
144.38(d)	26.2	3.0
146.39(d)	30.8	3.0
148.39(d)	35.8	1.8
150.39(d)	42.9	1.7
152.40(d)	48.3	1.6
154.40(d)	53.8	1.6

156.40(d)	61.3	1.7
158.41(d)	69.5	1.6
160.41(d)	76.6	1.6
162.41(d)	84.3	2.1
164.41(d)	92.4	2.4

were made, based upon the amount of hydrogen atoms in the target determined as described above and the p - p cross sections at small angles. The correction amounted to 1.4% for 8°.

In order to estimate the background counts due to the heavier nuclei, the relative differential cross sections for the protons elastically scattered by the impurity nuclei were measured from 8° to 30° laboratory angles, by accumulating the impurities in the evacuated chamber. The results were in agreement with those in the p - p check run in which the impurity peak due to heavier nuclei could be separated from the p - p peak up to 15°. They were also consistent with the assumption that the impurity atoms were oxygen mixed with small amount of nitrogen or carbon and that the cross sections for angles smaller than 15° were those due to Coulomb scattering¹⁴⁾. Thus, the background counts due to the heavier nuclei at small angles were estimated by extrapolating them, as in the case of the hydrogen components, from the angular region where the separated peaks were observed. The corrections amounted to 6% for 8° and 4.5% for 9° of the total counts, decreasing with increasing angle.

In addition to the above-mentioned backgrounds, some protons scattered by the structure in the scattering chamber entered the detectors. This background was measured by evacuating the target chamber and was found negligible for angles larger than 15°.

Uncertainties in these background subtractions, which were estimated to be 30 to 40% of the corrections, limited the accuracy of the results at the smallest angles.

For the recoil deuterons, the ambiguities in subtracting the background due to the break-up protons were estimated as upper limits to be 10% of the amount of the subtracted counts.

(b) Multiple scattering

Loss in beam charge collection due to multiple scattering in the target gas and in the foils of the target chamber was estimated to be 0.3% by the use of the Molière's theory¹⁵⁾ which includes single and plural scattering

effects. The error in this correction will be negligible. The effect of multiple scattering on the scattered particles to be detected was also estimated. It is considerably reduced by mutual compensation of the scattered-in and -out. An example of this compensation considered is schematically shown in Fig. 2. The corrections for incomplete -or over-compensation were estimated to be 1.4% at 8° , 0.5% at 9° and negligibly small at other measured angles for protons. They were also negligible for recoil deuterons. That the above-mentioned compensation is effective was partly evidenced by the results of the $p-p$ check run in which the measurements were carefully made with the two detectors of different geometry, I and II, at several angles from 15° to 30° , no difference being found within the experimental errors of 1 to 1.5%. In view of the approximate nature of the estimation, an error of 50% of this correction has been assumed.

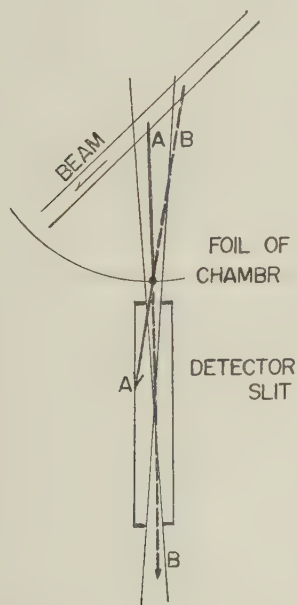


Fig. 2. Illustration of the compensation effect of scattered-in and-out particles.

A-A: scattered-out particle. B-B: scattered in particle.

(c) Slit-edge-penetration and -scattering

We have concluded as described in Sec. 3 (i) that most of the low-pulse-height counts were due to the slit-edge scattering and cut them off. But the particles scattered by the slit-edges contribute also to the main peak

above the cutoff threshold. The amounts of this contribution were estimated by the extrapolation from the counts per channel in the tail and subtracted. The corrections varied with angles from 0.4% to 1%. We also estimated them theoretically using the equation of Courant¹⁶⁾, the calculated being somewhat smaller than the experimental estimates. The error was taken to be half of the correction tentatively.

(d) Correction for inelastic scattering in the scintillator.

According to the recent investigation of D. H. Service at Minnesota¹⁷⁾, the effect of inelastic nuclear reactions in the scintillator which causes low-pulse-height counts can be neglected for the energy of the present work.

(e) Other errors

Accuracy of the measurement of the geometrical factors was 0.2% for each detector. Corrections for finite beam size and for finite angular resolution of the detector were made by the use of the relation of Critchfield¹⁸⁾.

The error in the alignment of the instruments relative to the incident beam is believed to be 0.03° . This causes, together with the error in reading of the graduation on the turn table, the uncertainty of 1.4% at 8° in the cross section, decreasing with increasing angle.

The error in measurement of the deuterium gas density was 0.25%, mainly due to the uncertainty in the correction for the impurity hydrogen described in Sec. 3 (i).

The error in the collected charge, consisting of errors in calibration of the integrator and of its zero drift, was 0.7%. The error arising from the neglect of the low-energy components of the incident beam was estimated to be less than 0.5% (Sec. 3 (i)).

The various errors considered above, together with the one due to the counting statistics, have been combined quadratically and are given in the third column of Table II as the estimated probable errors.

The uncertainty in the beam energy at the target center was 0.5%, including its fluctuation (Sec. 2 (iv)). The half-width of the energy spread was 0.5%.

(iv) Discussion

The results of the present work are compared with those of the 14.1 MeV $n-d$ scattering in Fig. 3.

In view of the fairly large quoted errors in the $n-d$ data, the cross sections for $p-d$ and $n-d$ scattering are in good agreement, although the $p-d$ cross sections seem to be systematically a little smaller than the $n-d$ cross sections at backward angles. The differences may be still larger if one takes account of

Table III. Differential cross sections for $p-d$ elastic scattering at 10.14 MeV.

θ c.m. (degrees)	σ c.m. (mb/steradian)	Probable error %
14.99	145.2	5.1
16.53	137.1	2.7
18.01	128.0	2.4
19.55	131.0	2.1
21.04	129.6	2.1
22.52	131.8	2.1
24.00	129.7	2.1
26.97	126.4	1.9
29.97	127.9	0.9
44.52	111.1	0.8

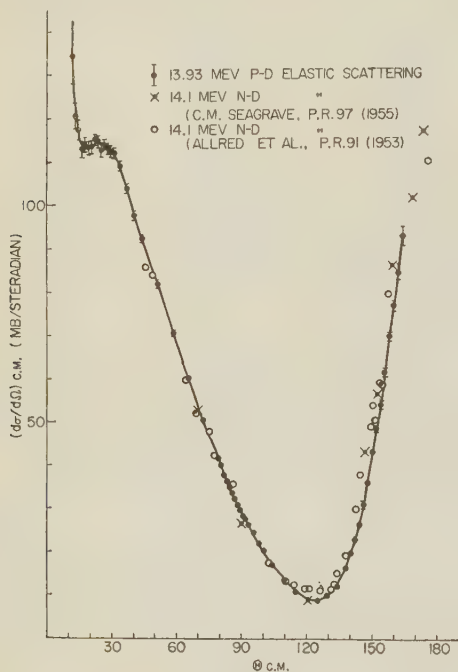


Fig. 3. Angular distribution of the protons elastically scattered by deuterons at 13.93 MeV.

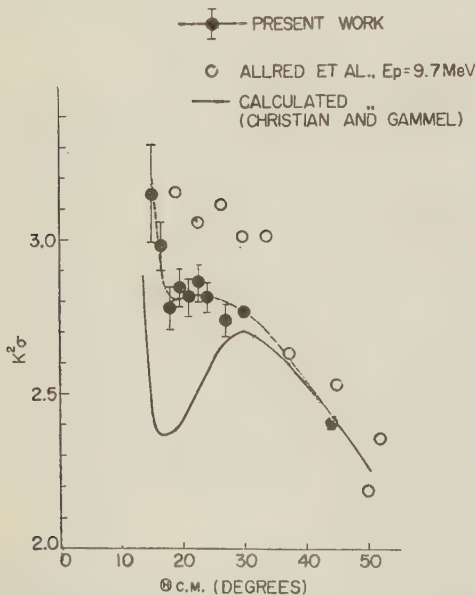


Fig. 4. Angular distribution for the $p-d$ elastic scattering at 10-14 MeV in the small angle region

the difference of 1.2% in the energy used. The experimental values of the cross section are considerably higher than the theoretical prediction of de Borde and Massey at the forward angles⁶⁾. As was mentioned by de Borde and Massey, the situation will be the same if one calculates according to the results of Christian and Gammel.

Since a similar discrepancy seems to exist at 9.7 MeV, as was mentioned in the Introduction, we measured the differential cross sections also at 10.14 MeV for the small angle region. The results are given in Table III. The energy of the incident protons was 10.14 ± 0.05 MeV. In Fig. 4, the results of the present work are compared with those at 9.7 MeV of Allred et al.⁸⁾. The theoretical curve taken from the paper of Christian and Gammel is also included. The results of Allred et al. seem to be systematically higher than ours by an amount outside the combined errors, even if the difference in the energy is taken into account. A similar tendency of the data of Allred et al. is found in the $p-p$ scattering experiment near 9.7 MeV, their results being higher than those of the recent work of Johnston and Young at Minnesota¹⁹⁾. According to the results of the present work, the discrepancy between theory and experiment has been reduced, but the experimental results are still higher than the theoretical and show no such distinctive Coulomb-nuclear interference minimum as predicted by the theory, which should be observed at least with the improved angular resolution of the present experiment.

These discrepancies between experiment

and theory for both 14 MeV and 10 MeV, may indicate that some deficit still exists in the assumptions or approximations which have been hitherto involved in the theory. In any case, a phase shift analysis of the data of the present work, making use of the method of Christian and Gammel will be valuable for the test of the existing theory.

§ 4. Proton-proton Scattering at 14.16 MeV

The experimental apparatus and procedures were the same as for the *p-d* experiment except the target gas. Commercial tank hydrogen was used as the target gas. Volumetric analysis showed that this gas consisted of 99.6% H₂, 0.25% N₂ and 0.15% O₂, other impurities being negligible. The determination of the amount of the impurities by the same method as described in detail in Sec. 3 was consistent with this result. Impurities owing to the evolution from the target chamber were also found. Since the primary purpose of the *p-p* experiment was the check of the *p-d* experiment, no effort to eliminate these impurities was made for the sake of time-saving.

The uncertainties in the corrections for the background due to these impurities affected considerably the accuracy of the results for the angles smaller than 15° in the laboratory

system, where the impurity peak could not be separated from the *p-p* peak.

The results are given in Table IV and in Fig. 5. The energy of the incident protons was 14.16± 0.07 MeV. In transforming the angle and the cross section from the laboratory to the center-of-mass system, the relativistic relations have been used.

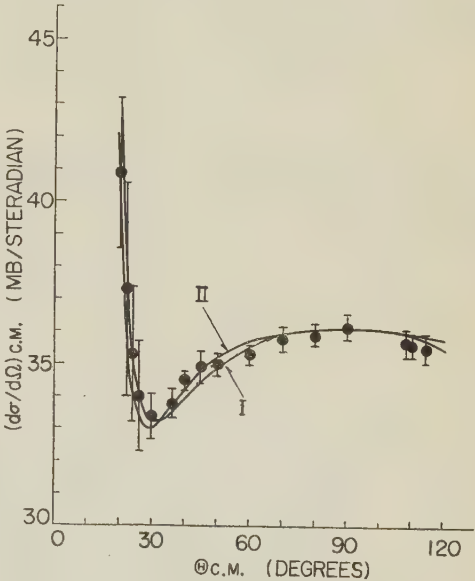


Fig. 5. Angular distribution for the proton-proton scattering at 14.16 MeV.

Curve I: Calculated with *S*-wave phase shift

$$^S\delta_0=54.0^\circ$$

Curve II: Calculated with

$$^S\delta_0=53.7^\circ, \ ^P\delta_0=3.51^\circ, \ ^P\delta_1=-3^\circ$$

$$^P\delta_2=1.2^\circ \text{ and } ^D\delta_2=0.2^\circ$$

Table IV. Proton-proton scattering cross sections at 14.16 MeV in the center-of-mass system.

θ c.m. (degrees)	σ c.m. (mb/steradian)	Probable error %
18.07	48.2	9.8
20.07	40.9	5.4
22.08	37.3	6.4
24.09	35.3	4.6
26.09	34.1	5.1
30.11	33.4	2.0
36.13	33.8	1.3
40.14	34.5	0.9
45.15	34.9	1.4
50.17	35.0	1.0
60.18	35.3	0.9
70.20	35.8	1.0
80.21	35.9	1.2
90.21	36.2	1.2
108.20	35.7	1.3
110.20	35.6	1.0
114.19	35.4	1.2

The various sources of error were carefully examined and the estimation of the errors given in the table was made with the similar procedures to those in the *p-d* experiment. Although the errors assigned to the cross section values for forward angles are somewhat large, the results for angles larger than 30° in the center-of-mass system are considered to have comparable accuracy to the existing data at other energy values between 9 and 21 MeV¹⁹⁾⁻²²⁾.

The angular distribution at 14 MeV appears to have rather a flat maximum at 90°, as in the case of 9.7 MeV¹⁹⁾, in contrast with the data at 18.2 MeV, in which it appears to have a flat minimum²¹⁾. But the accuracy of the experiments is not sufficient for definite con-

clusion. As is shown by the curve I in Fig. 5, the angular distribution is fitted fairly well with the S-wave phase shift alone, although the experimental curve shows a somewhat sharper interference minimum near 30° in the center-of-mass system.

No systematic phase shift analysis was attempted, but some qualitative informations on the P-wave phase shift are inferred. The differential cross section can be written in the S-, P- and D-wave approximation as²³⁾

$$k^2\sigma(\theta) = A_0({}^S\delta_0, {}^P\delta_2, \theta) + A_1(\theta)Z_1 \\ + A_2(\theta)Z_2 + A_3(\theta)Z_3,$$

where the parameters, Z_1 , Z_2 and Z_3 , are certain functions of the P-wave phase shifts, ${}^P\delta_0$, ${}^P\delta_1$, and ${}^P\delta_2$, and approximately expressed as

$$Z_1 = 9 < {}^P\delta^2 > = ({}^P\delta_0)^2 + 3({}^P\delta_1)^2 + 5({}^P\delta_2)^2,$$

$$Z_2 = 9 < {}^P\delta > = {}^P\delta_0 + 3{}^P\delta_1 + 5{}^P\delta_2$$

and

$$Z_3 = \frac{3}{2}({}^P\delta_1)^2 + \frac{7}{2}({}^P\delta_2)^2 + 4{}^P\delta_0{}^P\delta_2 + 9{}^P\delta_1{}^P\delta_2$$

for small values of the P-wave phase shifts. Explicit formulae of $A_i(\theta)$ are found in the literature. Except at extremely small angles, $A_1(\theta)$ is almost independent of angle and one can put $A_1(\theta) = 1$ for $\theta \geq 20^\circ$, with sufficient accuracy in our case. Further, it is seen that the shape of the function A_0 at $\theta \geq 20^\circ$ is also nearly independent of ${}^S\delta_0$ for its value between 45° and 55° . Consequently, if one assumes ${}^P\delta_2 = 0.2^\circ$ to 0.3° as expected from the current theory of nuclear forces, angular dependence of A_0 is fixed and a certain region in the Z_2 - Z_3 plane, inside of which the good fit to the experimental results is obtained, are determined from the experimental angular distribution between 20° and 90° , irrespective of the S-wave phase shift. Thus, we found that

$$|Z_2| < 0.2 (| < {}^P\delta > | < 1.3^\circ)$$

and

$$-0.05 < Z_3 < 0.03$$

namely the average P-wave phase shift is very small.

The curve II in Fig. 5 is an example which fits the experimental results with S-, P- and D-wave phase shifts.

More accurate data especially at small angles between 20° and 30° in the center-of-mass system will serve to determine the values of the above-mentioned parameters more de-

finitely, and even if a unique set of the phase shifts can not be obtained, as MacGregor has shown, an important information on the P-wave, and accordingly on the nuclear forces in the triplet odd states will be obtained.

Acknowledgements

The authors wish to thank the operating crew of the cyclotron, particularly Messrs. T. Karasawa, A. Suzuki and H. Ogawa. They also wish to express their thanks to Professor I. Nonaka for his constant encouragement.

References

- 1) The nuclear three-body problem has been surveyed by M. Verde in *Handbuch der Physik*, XXXIX pp 144-177. See also H. S. W. Massey: *Progress in Nuclear Physics*, (Pergamon Press) 235-270.
- 2) D. O. Caldwell and J. R. Richardson: *Phys. Rev.* **98** (1955) 28.
- 3) J. H. Williams and M. K. Brussel: *Phys. Rev.* **110** (1958) 136.
- 4) J. H. Coon and R. F. Taschek: *Phys. Rev.* **76** (1949) 710. J. C. Allred, A. H. Armstrong and L. Rosen: *Phys. Rev.* **91** (1953) 90. J. D. Seagrave: *Phys. Rev.* **97** (1955) 757.
- 5) R. S. Christian and J. L. Gammel: *Phys. Rev.* **91** (1953) 100.
- 6) A. H. de Borde and H. S. W. Massey: *Proc. Phys. Soc. London A*, **68** (1955) 769. R. A. Buckingham, S. J. Hubbard and H. S. W. Massey: *Proc. Roy. Soc. A*, **211** (1952) 183.
- 7) J. D. Seagrave and L. Cranberg: *Phys. Rev.* **105** (1957) 1816.
- 8) J. C. Allred et al.: *Phys. Rev.* **88** (1952) 433.
- 9) J. Iwadare et al.: *Supplement of the Progr. Theor. Phys.* **3** (1956) 32.
- 10) M. H. MacGregor: *Phys. Rev.* **113** (1959) 1559.
- 11) J. Sanada: *J. Phys. Soc. Japan* **14** (1959) 1463.
- 12) S. Kikuchi et al.: *J. Phys. Soc. Japan* **15** (1960).
- 13) The detector employed was similar to that of G. Igo and R. Eisberg: *Rev. Sci. Instr.* **25** (1954) 450.
- 14) For angles 20° and larger, the existing data could be used; C. Hu et al.: *J. Phys. Soc. Japan* **14** (1959) 861. S. Kobayashi: private communication. R. W. Peelle: *Phys. Rev.* **105** (1957) 1311.
- 15) H. A. Bethe: *Phys. Rev.* **89** (1953) 1256. G. Molière: *Z. Naturforsch.* **3a** (1948) 78.
- 16) E. D. Courant: *Rev. Sci. Instr.* **22** (1951) 1003.
- 17) Annual Progress Report, Univ. of Minnesota (1958).

- 18) D. O. Caldwell and J. R. Richardson: UCLA-22 (1954) (unpublished).
- 19) L. H. Johnston and D. E. Young: cited in ref 10.
- 20) B. Cork and W. Hartsough: Phys. Rev. **94** (1954) 1300.
- 21) J. L. Yntema and M. G. White: Phys. Rev. **95** (1954) 1226.
- 22) J. W. Burkig, J. R. Richardson and G. E. Schrank: Phys. Rev. **113** (1959) 290.
- 23) H. P. Noyes and M. H. MacGregor: Phys. Rev. **111** (1958) 223. E. Clementel and C. Villi: Nuovo Cimento **2** (1955) 1165.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 1, JANUARY, 1960

Investigation of the Reaction $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$

By Jiro MUTO

*Department of Nuclear Science, Faculty of Science,
Kyoto University*

(Received September 3, 1959)

The $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$ reaction was studied at the three resonances of 317, 392 and 437 kev proton energy. The level of Al^{26} , corresponding to the third excited state (3.97 Mev) in Mg^{26} , was found at 4.18 ± 0.02 Mev. Through the angular distributions of γ -rays, spins and parities of this level and some other levels were assigned as follows: 3.16 Mev, $J=2^+$; 4.18 Mev, $J=3^+$; 6.61 Mev, $J=3^-$; 6.68 Mev, $J=2^+$ or 3^+ ; 6.72 Mev, $J=4^+$ or 4^- . The second and third excited states in Mg^{26} were estimated to be $J=2^+$ and $J=3^+$ respectively. Excitation energies, the gamma decay scheme, and the radiation yield of the resonance levels are also given. The correspondence between levels of Mg^{26} and Al^{26} is discussed and a possible excited state configuration of Mg^{26} is suggested.

§ 1. Introduction

The energy levels of the nucleus Al^{26} , which is the central member of the isobaric triplets Mg^{26} , Al^{26} and Si^{26} , have been studied by many investigators. Swann, Mandeville and Whitehead¹⁾ reported the existence of three levels obtained from the energy measurements of neutrons from the reaction $\text{Mg}^{25}(d, n)\text{Al}^{26}$, whilst Browne²⁾ found five levels of Al^{26} in his accurate measurements of the reaction $\text{Si}^{28}(d, \alpha)\text{Al}^{26}$, in which reaction only $T=0$ states are expected to be reached. On the other hand, Endt, Kluyver and Van der Leun³⁾ have found seven levels by the study of γ -rays from the reaction $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$. They showed that the lowest level of 0.235 Mev is the $T=1$ level corresponding to the ground state of Mg^{26} , and that it decays to Mg^{26} by emitting positrons. By the analysis of the same reaction γ -rays, Kavanagh, Mills, and Sherr⁴⁾ have found a new level of 2.074 Mev which was considered

to be the second $T=1$ analogue level of the first excited state of 1.83 Mev in Mg^{26} . By a more extended study of the same reaction, Green, Singh and Willmott⁵⁾ have found five more levels and have shown that the 3.16 Mev level among them is the third $T=1$ level corresponding to the 2.97 Mev level of Mg^{26} . Recently Hinds and Middleton⁶⁾ have reported about sixty levels of Al^{26} from the investigation of the reactions $\text{Al}^{27}(\text{He}^3, \alpha)\text{Al}^{26}$ and $\text{Mg}^{24}(\text{He}^3, p)\text{Al}^{26}$, which includes the fourth $T=1$ level reported by us at about the same time.⁷⁾ In the present paper more details about our investigation will be given.

§ 2. Experimental Method

The Mg^{25} target was bombarded with the proton beam accelerated by the 600 KV Cockcroft-Walton type accelerator in Kyoto University. The energy spread of the proton beam analyzed by a 90° magnetic deflector was several kev at the energy of some hundred

kev. The isotopically enriched Mg^{25} target, which was in the form of a thin metallic film on a copper plate of 0.5 mm thickness, was made by using the isotope separator of Kyoto University³⁾. In order to avoid the γ -rays from the carbon-proton reaction, during the experiments the targets were replaced by new ones every few hours because the deposit of carbon on the target became gradually appreciable in 30 or 40 minutes in spite of the use of a liquid air trap on the path of proton beam. The current intensity of the proton beam used was 10~15 μA .

For the measurement of the γ -ray spectra, a large scintillation counter incorporating a 5'' $\times$ 4'' NaI(Tl) crystal and an EMI 6099B photomultiplier was used. The resolution thus obtained was better than that of previous studies of the same γ -ray spectrum, and the high efficiency of the large crystal made it possible to investigate the lowest resonance reaction which had a low γ -ray yield. To obtain the pulse height distribution, two types of pulse height analyser were used, i.e. a 10-channel kick-sorter of Johnston-type served for the energy determination of the γ -ray spectrum and a 100-channel kick-sorter of Hutchinson-Scarrott-type (Sunvic Co.) was used for intensity and coincidence measurements.

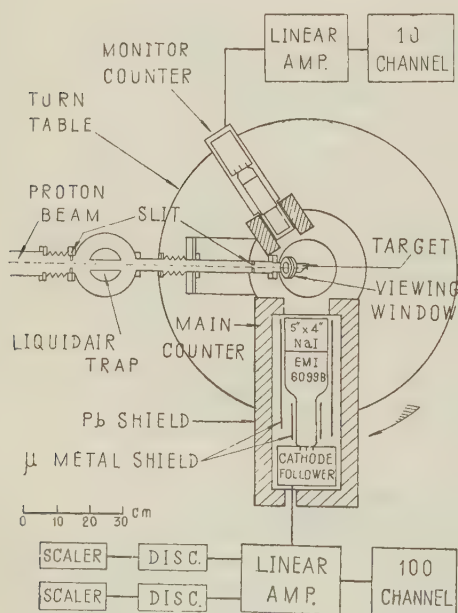


Fig. 1. Schematic view of the assembly for gamma-ray angular distribution measurements.

The scintillation counter was screened by 5 cm thick lead blocks from background radiation. These lead shields reduced the background to about 1/4 of its original intensity. The remaining soft γ -ray component, however, still proved troublesome in the analysis of the low energy part of the γ -ray spectrum. The counter was mounted upon a table which rotated about the target. The distance between the counter and the target was 150 mm. This arrangement is shown in Fig. 1.

§ 3. Measurement and Analysis

(1) Resonances

The γ -ray yield *versus* the energy of the bombarding proton is shown in Fig. 2. This yield contains only high energy γ -rays which exceed 3.2 Mev. The width of the groups is due to the target thickness as well as the energy spread of the proton beam.

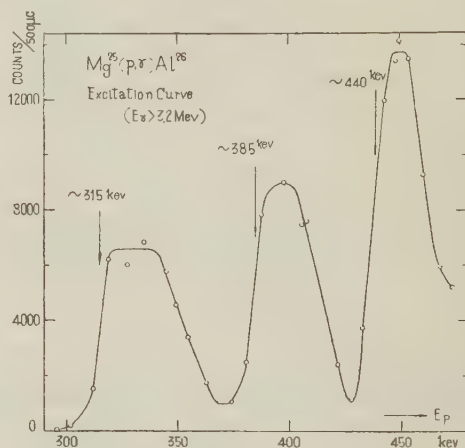


Fig. 2. Gamma-ray yield from the reaction $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$.

The aim of this excitation function was not so much the precise determination of the resonance energy, as the operating voltage of the high tension apparatus and the estimation of the absolute yield at each resonance. The absolute values of the voltage in Fig. 2 were calculated from the values of the voltage and loading current in the primary circuit of the high tension equipment, and the relative scale was calculated from the exciting current of the magnetic analyser.

The purity of the enriched Mg^{25} target seems to be high, because in the excitation curve the resonances due to the (p, γ) reaction from Mg^{26} was not obviously observed. This

should appear at energies of 338.5 ± 0.5 and 454.2 ± 0.3 kev.

The approximate resonance energies derived from our experiments are shown in Table I, and are compared with the previous results of other investigators. In the following, the values of the resonance energies as reported by Hunt *et al.* will be used.

Table I. The resonances in the $Mg^{25}(p, \gamma)Al^{26}$ reaction below 500 kev.

Author	Tangen ⁹⁾	Taylor <i>et al.</i> ¹⁰⁾	Kluyver <i>et al.</i> ¹¹⁾	Hunt <i>et al.</i> ¹²⁾	This work
detection method	γ and β^+	β^+	γ	γ and β^+	γ
proton	310 ± 3		321	316.7 ± 0.7	315
resonance	392 ± 4	388	395	391.5 ± 0.5	385
energy	430 ± 4		441	436.5 ± 0.4	440
in kev.	490 ± 5	494	501	495.6 ± 0.6	
		all ± 10 to 15	all ± 15		

(2) Analysis of γ -ray spectra

The pulse height distributions of the γ -rays at the three resonances 317 kev, 392 kev and 437 kev, using the 100-channel kick-sorter, are shown in Figs. 3, 4 and 5 respectively. In each resonance two pulse height distributions were taken at angles of 90° and 0° to the incident proton beam. These two distributions were normalized by a fixed monitor counter mounted at an angle of 270° or 240° to the

incident beam.

To obtain the γ -ray spectra from the pulse height distributions, the pulse height distribution of several different monochromatic γ -rays, listed below, was measured with the same geometry.

$$E_\gamma = 1.28 \text{ Mev from } Na^{22}(\beta^+ \text{ decay})$$

$$E_\gamma = 2.36 \text{ Mev from } C^{12}(p, \gamma)N^{13}$$

$$\text{at } E_p \sim 450 \text{ kev}$$

$$E_\gamma = 4.43 \text{ Mev } \} \text{ from } B^{11}(p, \gamma)C^{12}$$

$$E_\gamma = 11.67 \text{ Mev } \} \text{ at } E_p \sim 300 \text{ kev}$$

$$E_\gamma = 6.14 \text{ Mev from } F^{19}(p, \alpha, \gamma)O^{18}$$

$$\text{at } E_p \sim 350 \text{ kev.}$$

These are presented in Fig. 6. It is seen that the pulse height distribution of the monochromatic γ -rays of energies from 3 to 7 Mev has three peaks; the full energy peak, one-quantum escape peak and a two-quantum escape peak. The γ -rays higher than 10 Mev, however, give a single peak at the position corresponding to the escape of one quantum.

The analysis of the γ spectrum from $Mg^{25}(p, \gamma)Al^{26}$ has been performed by "peeling off" successive γ -ray spectra from the high energy end of the total spectrum. The spectrum of an individual γ -ray was determined from the nearest monochromatic calibration γ -rays by interpolation and by normalizing to the full energy peak.

By this procedure we were able to find small γ -ray components which showed no peaks in the total pulse height distribution.

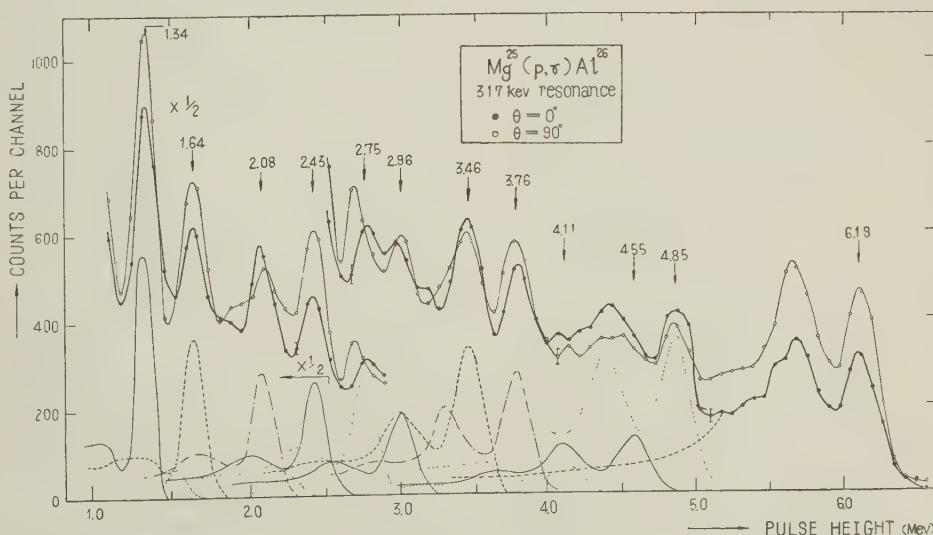


Fig. 3. The scintillation spectra taken at the 317 kev resonance at 0° and 90° to the proton beam. The dotted curves show the pulse spectra of individual gamma-rays into which the 0° degree spectrum was decomposed.

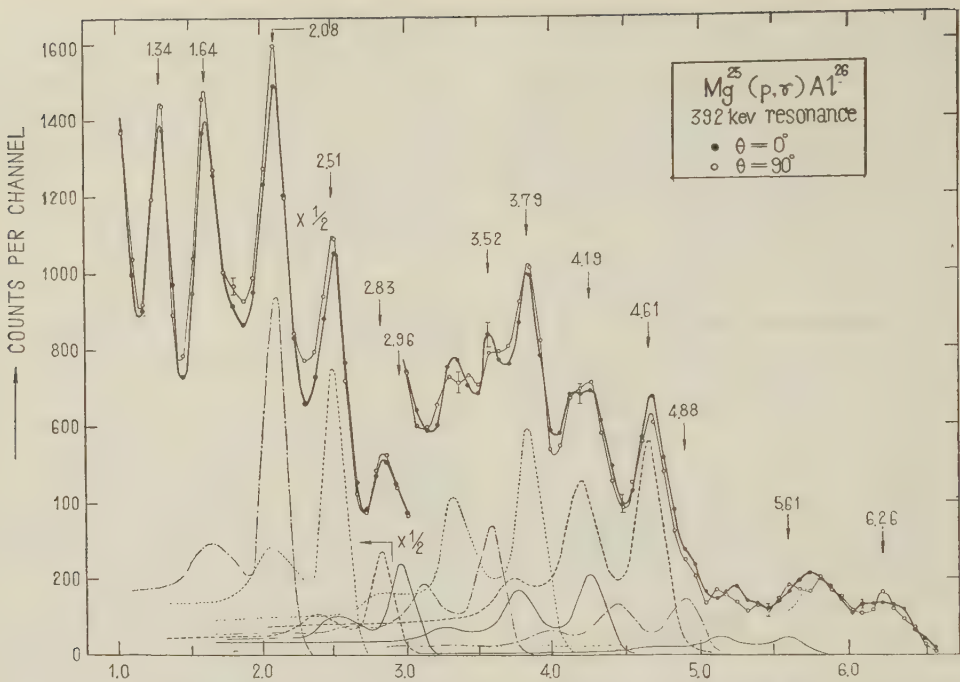


Fig. 4. The scintillation spectra taken at the 392 kev resonance at 0 and 90 degrees to the proton beam. The dotted curves show the pulse spectra of individual gamma-rays into which the 0 degree spectrum was decomposed.

However, it should be admitted that this method is liable to possible error. The component γ -rays deduced by this method are shown in Figs. 3, 4 and 5.

For the γ -rays with energies above 5 Mev, the position of their one-quantum escape peak, the highest peak for these γ -rays, was used for the energy determination. The position

of this peak plus 0.51 Mev was found to be linear up to 10 Mev. In case when the γ -ray spectrum was very complicated, the peak position of a γ -ray sometimes appeared slightly shifted in the total spectrum, due to the effect of the neighbouring γ -rays. The real position of the peak was found by the "peeling off" procedure.

The relative intensities of every γ -ray component were calculated by using the table¹³⁾

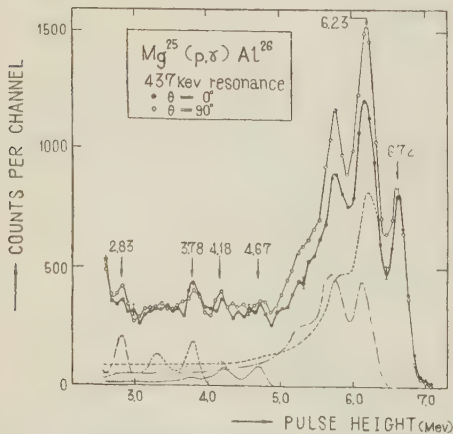


Fig. 5. The scintillation spectra taken at the 437-kev resonance at 0 and 90 degrees to the proton beam. The dotted curves show the pulse spectra of individual gamma-rays into which the 0 degree spectrum was decomposed.

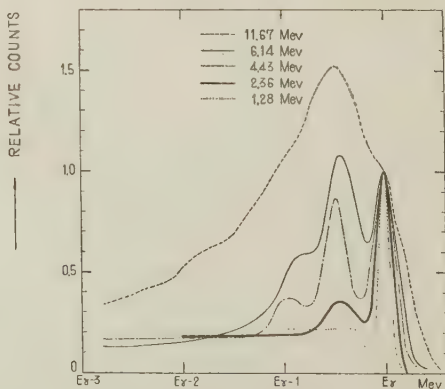


Fig. 6. Standard gamma-ray spectra measured with a NaI crystal, 5 inches in diameter and 4 inches high, normalizing the relative value of the intensity at full energy peak.

Table II. Gamma-rays observed at the 317 kev resonance.

E_γ (MeV)	Transition	Relative intensity	Anisotropy A_2
6.19*	6.61→0.42	32.5±3.3	-0.26±0.025
4.85±0.05	6.61→1.76	18.3±2.1	0.20±0.06
4.55±0.04	6.61→2.07	6.4±1.9	0.20±0.14
4.11±0.06	6.61→2.54	3.3±1.4	0.10±0.24
3.76±0.04	4.18→0.42	16.5±2.1	-0.21±0.07
3.46±0.03	6.61→3.16	12.8±2.1	0.19±0.10
2.96±0.04	(6.61→3.68)	7.2±1.3	
2.75±0.04	3.16→0.42	10.8±1.4	
2.43±0.03	6.61→4.18	20.3±2.5	-0.27±0.06
2.08±0.02	{2.54→0.42 3.16→1.06}	11.1±2.5	
(1.80±0.04)**	—	(3.3±1.0)	
1.64±0.03	{2.07→0.42 (3.68→2.07)}	16.4±2.3	
1.35±0.015	1.76→0.42	20.5±2.7	
1.07±0.01	3.16→2.07	4.7±0.9	
1.007±0.01	2.07→1.06	6.8±1.4	
0.838±0.008	1.06→0.23	13.1±2.2	
0.418±0.005	0.42→0	—***	
1.40	3.16→1.76	<2.1	
0.511	annih. rad.	—***	

*: accepted standard γ -ray.

**: existence doubtful.

***: not accurately measured.

Table III. Gamma-rays observed at the 392 kev resonance.

E_γ (MeV)	Transition	Relative intensity	Anisotropy A_2
6.26*	6.68→0.42	9.0±0.9	0.04±0.04
(5.61±0.06)**	6.68→1.06	2.2±1.1	
4.88±0.05	6.68→1.76	6.3±1.7	0.035±0.04
4.61±0.05	6.68→2.07	20.5±2.4	
4.19±0.04	6.68→2.54	7.7±2.5	
3.79±0.04	4.18→0.42	19.1±2.7	
3.52±0.03	6.68→3.16	9.8±3.0	
(2.96±0.04)**	6.68→3.75	5.8±2.3	
2.83±0.03	{4.59→1.76 3.16→0.42}	11.8±2.1	
2.51±0.02	{6.68→4.18 4.59→2.07 2.54→0}	30.9±3.7	
2.08±0.02	{6.68→4.59 2.54→0.42 3.16→1.06}	31.8±5.7	
1.79±0.04	{(3.76→1.85) (1.85→0)}	12.2±3.4	
1.64±0.015	2.07→0.42	14.0±4.6	
1.34±0.02	1.76→0.42	12.3±3.6	
1.083±0.015	3.16→2.07	16.6±4.1	
1.01±0.01	2.07→1.06		
0.839±0.007	1.06→0.23	28.7±4.1	
0.418	0.42→0	—***	
2.36	C^{12} contamination	very weak	
0.511	annih. rad.	—***	

*: accepted standard γ -ray.

**: existence doubtful.

***: not accurately measured.

of calculated efficiency of NaI(Tl) and are listed, together with their energies, in Tables II, III and IV. These values of intensity are normalized to the total decay from the resonance level as 100.

(3) Angular distributions

The spectrum of the γ -rays was obtained with the large crystal counter placed at a distance of 15 cm from the target at angles of 90° and 0° to the proton beam. The small crystal counter at a fixed position served as a monitor. The pulse height distributions at the three resonances are shown in Figs. 3, 4 and 5. The relative intensity of each γ -ray component was determined and the anisotropies of some of the γ -rays were calculated. In Tables II, III and IV they are presented in the form of coefficient A_2 , assuming the angular distribution to be of the form $W(\theta) = 1 + G_2 A_2 P_2(\cos \theta)$, with $G_2 = 0.916$. The errors of these A_2 values are caused mainly by the statistical errors of the number of counts. Another source of error arising from the procedure of decomposing the pulse height distributions in different ways was also con-

sidered, but this source of error was found to be less than, or nearly equal to, the statistical error, by employing several trial procedures of decomposition. The relative intensities of the γ -ray components used in the calculation of the anisotropies were corrected for the finite solid angle subtended by the counter (factor G_2) and the absorption effects of the target backing materials.

(4) Coincidence spectrum

In order to determine the decay scheme for many γ -rays, especially for some of the γ -rays involving the level and decay mode not previously reported, coincidence spectra were taken. One of them in the case of the 392-kev resonance is illustrated in Fig. 7. These pulse height distributions were obtained from the large crystal counter with the 100-channel kick-sorter which was gated by the pulse from the small crystal counter and single channel analyser. The resolving time of the coincidence arrangement was $2\tau \approx 6\mu$ sec.

In the interpretation of coincidence spectra, care was needed to exclude coincidences from the "Compton tails" of the γ -rays of energy

Table IV. Gamma-rays observed at the 437 kev resonance.

E_γ (Mev)	Transition	Relative intensity	Anisotropy A_2
6.72*	6.72→0	45.9±4.6	-0.09±0.04
6.23±0.07	6.72→0.42	29.3±4.9	-0.19±0.05
(5.61±0.07)**	6.72→1.06	2.4±1.7	
4.67±0.05	6.72→2.07	3.5±1.5	
4.18±0.04	6.72→2.54	5.1±1.4	
3.78±0.04	4.18→0.42	4.8±1.2	
(3.05±0.06)**	(6.72→3.75)	2.5±1.8	
2.83±0.03	4.59→1.76	3.6±1.0	
2.54±0.03§	6.72→4.18	—****	
2.10±0.04	{6.72→4.59 2.54→0.42}	12.0±6.0	
(1.85±0.03)**	{(3.75→1.85) (1.85→0)}	4.7±4.7	
1.644±0.01***	2.07→0.42	4.3±3.3	
1.346±0.01***	1.76→0.42	3.6±2.4	
1.009±0.008***	2.07→1.06	4.3±1.8	
0.839±0.007***	1.06→0.23	6.9±1.7	
0.418±0.005***	0.42→0	—****	
2.37	C ¹² contamination	strong	
0.511	"	"	

* : accepted standard γ -ray.
** : existence doubtful.
*** : mean value in the three resonances.
**** : not accurately measured.
§ : measured in coincidence with 3.8 Mev γ -ray, as the 2.2-2.6 Mev region was obscured by a strong C¹².p γ -ray in the singles spectra.

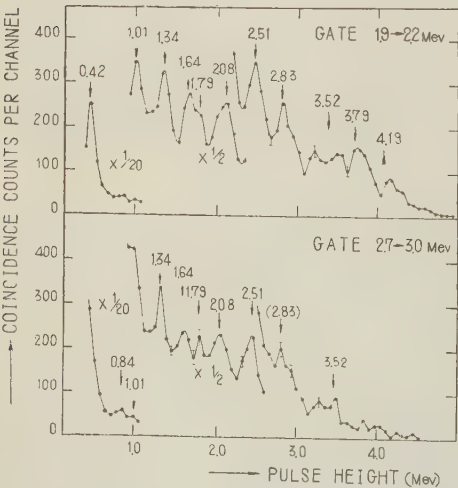


Fig. 7. Spectra in coincidence with the 2.08 Mev γ -ray and 2.83 Mev γ -ray, taken at the 392 kev resonance.

higher than the ones in question.

The two γ -rays of 2.43 Mev and 3.76 Mev obtained in the case of the 317 kev resonance were found to be in cascade from their coincidence nature, and the fact that the sum of these two energies is equal to the energy difference between the resonance level (6.61 Mev) and the second excited level (0.42 Mev) suggested the existence of a new level at either 2.85 Mev or 4.18 Mev above the ground state. To distinguish between the two possibilities, the energy shifts of these γ -rays in the case of three different resonances were measured. It was found that the energy of 2.5 Mev γ -ray changed, whilst the energy of the 3.8 Mev γ -ray remained constant. These energies are presented in Table V, and the coincidence spectra of the 2.5 Mev γ -rays at the three resonances are shown in Fig. 8. From these experimental facts the existence of a level of 4.18 Mev above the ground state could be concluded. This level is considered

Table V.

Reso- nance	Excitation energy	Energy of γ -ray	
		2.5 Mev	3.8 Mev
317 kev	6.61 Mev	2.43±0.03 Mev	3.76±0.04 Mev
392 kev	6.68 Mev	2.51±0.02 Mev	3.79±0.04 Mev
437 kev	6.72 Mev	2.54±0.03 Mev	3.78±0.04 Mev

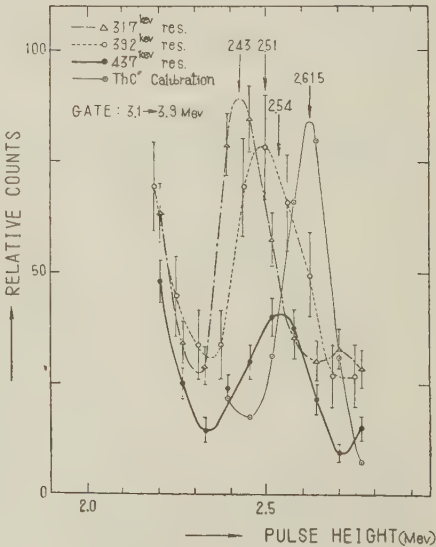


Fig. 8. 2.5 Mev parts of the coincidence spectra gated by the 3.8 Mev γ -ray, taken at the three different resonances, showing the energy shift of the 2.5 Mev γ -ray together with the 2.615-Mev calibration line of ThC',

to be the $T=1$ level expected at an excitation of about 4.20 Mev,¹⁴⁾ corresponding to the 3.97-Mev level in Mg^{26} .

§ 4. Discussion

Decay scheme

The number of γ -ray components observed in this experiment is more than in those previously reported, but almost all of the γ -rays could be fitted to the level scheme previously proposed,⁵⁾ apart from the newly introduced level of 4.18 Mev, which had not been known before the work of Hinds and Middleton⁹⁾ reported quite recently.

To determine the decay mode of the resonance level, we have considered the energies and the relative intensities of the γ -rays as well as the interpretation of coincidence spectra. As the decay mode of the lower levels, we have mainly adopted that proposed by Green *et al.*⁵⁾ on the bases of a number of coincidence measurements. These previous assignments were almost consistent with our γ -ray energies, relative intensities and coincidence spectra, except for a few cascades.

The γ -ray cascade involving the 4.18 Mev level has been mentioned in the previous section. Recent measurements of Hinds and Middleton indicate the existence of doublet levels at 4.191 ± 0.010 and 4.202 ± 0.010 Mev,

the former probably corresponding to our 4.18 Mev level which was found by us independently.

The 2.83 and 2.52 Mev γ -rays observed at the 392 kev resonance were assigned to transitions from the 4.59 Mev level to the 1.76 and 2.07 Mev levels. This was concluded from the observed intensities and was checked with the coincidence measurements. The 4.55 Mev level was previously found and reported to decay with γ -rays of 3.50 and 4.14 Mev to the 1.07 and 0.42 Mev levels.⁵⁾ At the 392 kev resonance, γ -rays of this energy were observed, but the assignment of these γ -rays to transitions from the resonance level to the 3.16 and 2.54 Mev levels was preferable from the analysis of coincidence spectra. Their 4.55 Mev level may correspond to the 4.541 ± 0.010 Mev level reported by Hinds and Middleton, and then our 4.59 Mev level probably corresponds to the Hinds' 4.595 ± 0.010 Mev level.

The 1.40 Mev γ -ray, previously assigned to transitions from the 3.16 Mev level to the 1.76 Mev level with a branching ratio of 12% of the decay of the 3.16 Mev level, was not positively observed, and was less than 8% in our measurements.

The cascades involving the 2.07 Mev level will be discussed later. The decay scheme

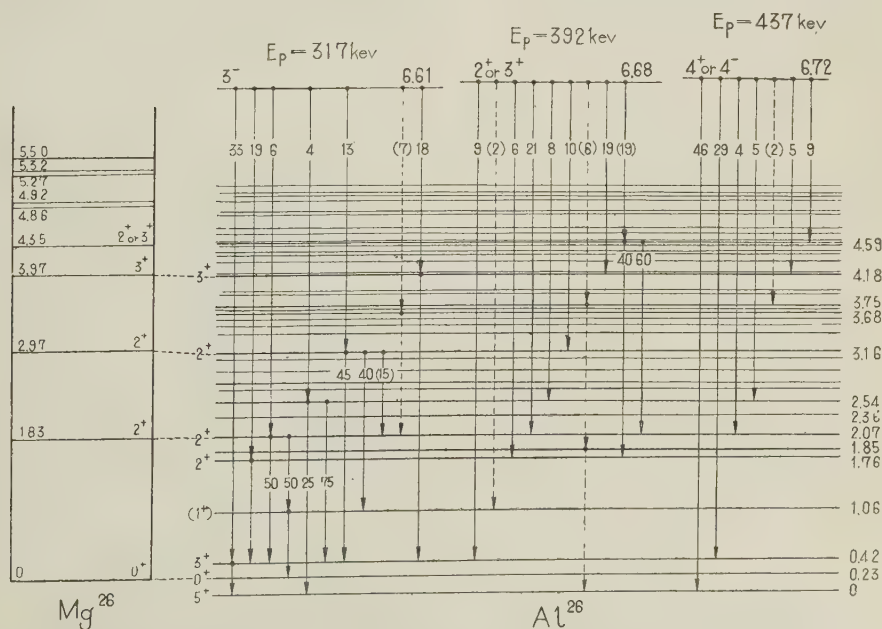


Fig. 9. Level scheme of Al^{26} together with that of Mg^{26} . Excitation energies, the gamma-ray decay scheme and relative branching ratios in Al^{26} are illustrated.

thus obtained is shown in Fig. 9.

The energies of every level were computed from the energies of the γ -rays, which were measured within an experimental error of 1%

Table VI. Excitation energies of the levels in Al^{26} (in Mev).

Excited states	(1)	(2)	(3)	(4)
1	0.229	0.229 ± 0.003	0.23	(0.229)
2	0.416	0.418 ± 0.002	0.42	0.418 ± 0.005
3	1.052	1.060 ± 0.002	1.07	1.068 ± 0.009
4	1.755	1.762 ± 0.003	1.76	1.764 ± 0.015
5	1.846	1.853 ± 0.003	1.86	
6	2.067	2.073 ± 0.003	2.08	2.070 ± 0.015
			2.09	
7	2.362	2.368 ± 0.003	2.32	
8	2.542	2.548 ± 0.004	2.54	2.51 ± 0.003
13	3.155	3.160 ± 0.006	3.16	3.15 ± 0.02
17	3.675		3.67	
19	3.746		3.76	
22	4.191			4.18 ± 0.02
23	4.202			
27	4.541		4.55	
28	4.595			4.59 ± 0.02
29	4.613			

- (1) Hinds and Middleton, reference 6 (1959), from the $\text{Al}^{27}(\text{He}^3, \alpha)\text{Al}^{26}$ and $\text{Mg}^{24}(\text{He}^3, p)\text{Al}^{26}$ reactions. The experimental error is ± 10 kev.
(2) Browne, reference 19 (1959), from the $\text{Si}^{28}(d, \alpha)\text{Al}^{26}$ reaction.
(3) Green, Singh and Willmott, reference 5 (1956), from the $\text{Mg}^{26}(p, \gamma)\text{Al}^{26}$ reaction.
(4) Present investigation from the $\text{Mg}^{26}(p, \gamma)\text{Al}^{26}$ reaction.

and calibrated by using the energies of the standard γ -rays from Na^{22} (1.277 Mev) and ThC'' (2.615 Mev), and also using the energies of the $\text{Mg}^{26}(p, \gamma)\text{Al}^{26}$ reaction γ -rays, as cited in Tables II-IV. The energies of the third and seventh excited levels were determined from the energy of the first excited state which was reported as 0.229 ± 0.003 Mev.¹⁶⁾ The energies of these excited states have also been measured by other investigators, and especially Hinds and Middleton⁶⁾ recently reported many more excited levels than had previously been known, the energies of which were obtained with high precision by magnetic analysis of α -particles and protons from the reactions $\text{Al}^{27}(\text{He}^3, \alpha)\text{Al}^{26}$ and $\text{Mg}^{24}(\text{He}^3, p)\text{Al}^{26}$. Our values deduced from the γ -ray energies are compared in Table VI with these more precise energies, and both results coincide fairly satisfactorily with each other within the experimental error, which in turn supports the transition assignments listed in Tables II-IV.

Spin and Parity

From the anisotropy A_2 of the γ -rays, assuming the angular distributions of the form: $W(\theta) = 1 + G_2 A_2 P_2(\cos \theta)$, the spin and parity of the levels concerned were assigned.

The theoretical values of A_2 for some possible cases were calculated,¹⁶⁾ assuming a pure multipole transition. They are presented in Table VII.

At the 317 kev resonance, the 6.19 Mev γ -

Table VII. Theoretical anisotropy (A_2).

Proton orb. l_p	ang. mom.	Spin of res. level J_r	Channel spin J_c	Anisotropy A_2 for the final state of spin			
				$J_f=2$	$J_f=3$	$J_f=4$	$J_f=5$
0		2+	2	0.0000	0.0000	0.0000	—
		3+	3	0.0000	0.0000	0.0000	0.0000
		1-	2	-0.0100	0.0143	—	—
		2-	2	-0.3500	0.1000	—	—
		2-	3	0.1000	-0.0286	—	—
		3-	2	-0.2400	0.3000	-0.1000	0.1429
1		3-	3	0.3000	-0.3750	0.1250	-0.1786
		4-	3	0.2806	-0.1964	0.2750	-0.1000
		0+	2	0.0000	—	—	—
		1+	2	0.0500	-0.0714	—	—
		1+	3	-0.0143	0.0204	—	—
		2+	2 or 3	<i>s</i> -wave ($l_p=0$) predominant			
2		3+	2 or 3				
		4+	2	0.3733	-0.2806	0.3929	-0.1429
		4+	3	0.1341	-0.0281	0.0393	-0.0143
		5+	3	—	0.3341	-0.2476	0.3741

ray leading to the 0.42 Mev $J=3^+$ level has $A_2 = -0.26 \pm 0.025$, and the 4.85 and 4.55 Mev γ -rays leading to the 1.76 and 2.07 Mev levels, both known to be $J=2^+$,⁶⁾ have $A_2 = 0.20 \pm 0.06$ and 0.20 ± 0.14 , respectively. If we consider only pure multipole transitions, these values can uniquely be fitted with the theoretical values for $J_r=3^-$, due to p -wave capture, with the channel spin mixing ratio of $t=0.21 \pm 0.05$. Here t is the fraction of states formed by the channel spin $J_c=2$ to states formed by $J_c=3$. If we take into account the admixture of higher multipole component for these γ -rays, the experimental anisotropies can also be fitted with the theoretical predictions for $J_r=4^+$ and $J_r=4^-$. In the case of $J_r=4^+$, about 10% admixture of $E2$ component of $M1$ is necessary, and the d -wave capture at this low proton energy seems to be improbable. The $J_r=4^-$ assignment requires admixture of $M2$ component to $E1$, and the $M2$ transitions with an $E3$ admixture, which seem to be unlikely in view of the fact that the angular distributions of γ -rays measured at higher resonances by Green *et al.*⁵⁾ show almost pure $E1$ character. So we have assigned this resonance level as $J_r=3^-$, which is considered to be the most probable.

Using these values of the resonance spin and channel spin mixing ratio, the anisotropies of dipole transition γ -rays from the resonance level to the final states $J=2, 3$ and 4 are calculated to be $A_2 = 0.206, -0.258$, and 0.086 , respectively. The measured anisotropies of γ -rays leading to the 3.16 and 4.18 Mev levels from the resonance level have A_2 values of 0.19 ± 0.10 and -0.27 ± 0.06 , respectively, so it is natural to assume these levels as $J=2$ and 3 , respectively, fed from the resonance level by the strong almost pure dipole transitions. A small possibility of $J=4$ for the 3.16 Mev level remains of course, only from these considerations. On the other hand, these two levels in Al^{26} are considered to have $T=1$ character and to correspond to the second and third excited levels in Mg^{26} , mainly from their excitation energies. Further discussions about this point will be given later. Then, since the second and third excited levels in Mg^{26} have been assigned¹⁷⁾ as either 2^+ or 3^+ from the stripping reaction $Mg^{26}(d, p)Mg^{26}$, our A_2 values indicate that the 3.16 and 4.18 Mev levels must be $J=2^+$ and 3^+ , respectively, if the

$T=1$ assignments are confirmed. In this case, it follows that the second excited state in Mg^{26} is $J=2^+$, and the third excited state 3^+ . This $J=2^+$ assignment for the second excited state is consistent with the presence of the 2.97 Mev direct ground state transition γ -ray from this state, following the electron capture decay of Al^{26} .¹⁸⁾ To conclude, we consider it very probable that the 3.16 and 4.18 Mev levels have $T=1$ character and have spin and parity of 2^+ and 3^+ , respectively.

At the 392 kev resonance, all γ -ray angular distributions are isotropic within the experimental error. So we have assumed this resonance level to be either 2^+ or 3^+ , due to s -wave capture, although the possibility of $J_r=2^-$ or 3^- with an appropriate channel spin mixing ratio cannot be excluded.

At the 437 kev resonance, the anisotropies of two strong γ -ray components to the ground state of $J=5^+$ and the second excited state of $J=3^+$ are $A_2 = -0.09 \pm 0.04$ and -0.19 ± 0.05 respectively. These values agree with the calculated values of $A_2 = -0.100$ and $A_2 = -0.196$ in the case of $J_r=4^-$, and also with the values of $A_2 = -0.088 \pm 0.03$ and $A_2 = -0.190 \pm 0.05$ in the case of $J_r=4^+$, with the channel spin mixing ratio $t=1.9^{+3.3}_{-1.1}$. Unfortunately, unique assignment cannot be given from our experimental informations.

Table VIII. Resonance strength for three $Mg^{25}(p, \gamma)Al^{26}$ resonances.

Resonance (kev)	J_r	$(2J_r+1) \frac{\Gamma_p \Gamma_\gamma}{\Gamma_p + \Gamma_\gamma}$ (ev)	$\frac{\Gamma_p \Gamma_\gamma}{\Gamma_p + \Gamma_\gamma}$ (ev)
317	3	0.36 ± 0.07	0.051 ± 0.010
392	or $\frac{2}{3}$	0.64 ± 0.13	or $\frac{0.128 \pm 0.026}{0.091 \pm 0.018}$
437	4	0.69 ± 0.14	0.077 ± 0.015

Radiation yield

From the thick target yield of γ -rays from the resonance level, the quantity $(2J_r+1)\Gamma_p\Gamma_\gamma/(\Gamma_p+\Gamma_\gamma)$ was calculated, where J_r is the spin of the resonance level, Γ_p is the proton width and Γ_γ is the radiation width of the resonance level. These are given in Table VIII. These values agree fairly well with the previous results.³⁾

The level doublet at 2.07 Mev

The existence of a 2.06 Mev level was first shown by Browne²⁾ (1954) who studied the reaction $Si^{28}(d, \alpha)Al^{26}$ which is considered to

lead only to $T=0$ states of the final nucleus. Al^{26} should be expected to have a $T=1$ level in the neighbourhood of 2 Mev, corresponding to the first excited state of Mg^{26} . Kavanagh, Mills and Sherr⁴¹ (1955) suggested the existence of a $T=1$ level at 2.074 Mev in addition to the 2.064 Mev level, reported by Browne. This was also supported by Green, Singh and Willmott⁵¹ (1956) who assigned energies of 2.09 and 2.08 Mev to this doublet, with a definite separation of 10 kev. These authors proposed the level doublet from their study of the γ -ray spectra from the $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$ reaction, and the existence of this doublet was based upon the change of the decay mode of the 2.07 Mev level (1.64 and 1.01 Mev γ -rays) from resonance to resonance. The γ -rays leading to these levels could not be resolved in their experiments, of course, and the transition assignment of the low energy γ -rays may not be free from some doubt in view of the very complicated level structure of Al^{26} . Our experimental results do not necessarily postulate the existence of the doublet, proposing about equal transition rate of the 2.07 Mev level to the 0.42 and 1.06 Mev levels.

The recent analysis of the $\text{Si}^{28}(d, \alpha)\text{Al}^{26}$ reaction by Browne,¹⁴⁾ in which many more levels of Al^{26} were obtained up to the 3.6 Mev, has re-assigned the energy of the previously reported 2.064 Mev level which now becomes 2.073 ± 0.003 Mev. The recent study of the $\text{Al}^{27}(\text{He}^3, \alpha)\text{Al}^{26}$ and $\text{Mg}^{24}(\text{He}^3, p)\text{Al}^{26}$ reactions by Hinds and Middleton, which should indicate both $T=1$ and $T=0$ levels, agrees very closely with the level scheme proposed by Browne. No extra levels other than those found by the (d, α) reaction are indicated, and their 2.067 ± 0.010 Mev level has no doublet structure with separation greater than 4 kev. The level scheme proposed by Hinds and Middleton has been verified by Taylor, de Barros *et al.*¹⁹⁾ from a study of the same $\text{Al}^{27}(\text{He}^3, \alpha)\text{Al}^{26}$ reaction, with magnetic analysis. In this experiment it is of interest to note that the 2.07 Mev level has at least twice the strength of neighboring transitions.¹⁹⁾

If the significance of the $\text{Si}^{28}(d, \alpha)\text{Al}^{26}$ experiment of Browne is to be taken literally, it would suggest that there are in fact no $T=1$ levels in Al^{26} up to an excitation of

3.596 Mev, apart from the 0.229 Mev level which had only 10% of the intensity of the ground state transition and which is claimed to be the $T=1$ level corresponding to the ground state of Mg^{26} .

There seems to be no obvious answer to this difficulty other than supposing fairly large isobaric spin impurity for the $T=1$ level in question which is then not inhibited in the $\text{Si}^{28}(d, \alpha)\text{Al}^{26}$ reaction.

The same argument may also have to be applied to the 3.16 Mev level, which is fed by the α -particles from the (d, α) reaction fairly significantly, in spite of its assumed $T=1$ character.

The 4.18 Mev level

Referring to the energy level scheme reported by Hinds and Middleton, it may be that either the 4.191 Mev level or the 4.202 Mev level in Al^{26} is the analogue level to the third excited state of Mg^{26} . The 4.18 Mev level in this paper, which perhaps corresponds to their 4.191 Mev level, is considered to be the $T=1$ level in question¹⁴⁾ on the following grounds.

By the isobaric spin selection rule,^{20), 21)} the dipole transition with no change of isobaric spin in self-conjugate nuclei may be expected to be small. One might expect therefore the 317 kev and 392 kev resonance levels to be $T=0$ levels, due to their reasonably strong γ -decay to the assumed $T=1$ levels at 3.16 Mev and 2.07 Mev in Al^{26} .¹⁴⁾

Conversely, assuming that these resonance levels are $T=0$, one may expect strong transitions to $T=1$ levels of the final nucleus. The strength of the γ -decay in the observed spectrum leading to the 4.18 Mev level then suggests that this is a $T=1$ state.

If one assumes the Mg^{26} configuration to be $(d_{5/2})^{-2}$, this would require a spin sequence $J=0^+, 2^+, 4^+$, and assuming the ground state and 1.83 Mev level of Mg^{26} to correspond to the 0^+ and 2^+ states respectively, the 2.97 Mev level of Mg^{26} would need to be 4^+ in consistent with this picture, whilst experimentally it is assigned to be $J=2^+$. In addition, the 4.18 Mev level of Al^{26} is indicated to have spin 3 from our experiment and this implies that the 3.97 Mev level of Mg^{26} would also be 3^+ . This assignment is not possible on the pure jj -coupling scheme assuming $T=1$.

If we assume the excited state configuration of Mg^{26} to become $(d_{5/2})^{-3}(s_{1/2})^1$ from, say, 2.5 Mev upwards, implying an $(s_{1/2})$ admixture, this would permit $J=2^+$ and $J=3^+$ for the 2.97 Mev and 3.97 Mev levels with $T=1$.

The introduction of the mixed configuration between the 1.83 Mev and 2.97 Mev levels is based on the fact that the 1.83 Mev level excitation has been satisfactorily calculated by Thieberger and Talmi²²⁾ on the pure jj -coupling scheme, using parameters which also give good agreement for a wide range of nuclei.

Although the introduction of the $(d_{5/2})^{-3}(s_{1/2})$ configuration is suggested tentatively, it would permit understanding of the level spins of Mg^{26} . By introducing into Al^{26} a similar configurational mixing, states with $J=2^+$ or 3^+ may be obtained with either $T=1$ or $T=0$. The spin correspondence between levels of Mg^{26} and Al^{26} would then follow without reference to the isobaric spin of the Al^{26} states.

Acknowledgements

The author expresses his cordial thanks to Prof. K. Kimura and Prof. T. Shidei of Kyoto University for their support and encouragement throughout the present work. He is also deeply indebted to his collaborators Mr. K. Okano and Mr. T. Tabata for their indispensable aid during the whole experiment, and to Dr. M. Umezawa, Mr. I. Taylor and Mr. F. de Barros of Manchester University for helpful conversations. He also wishes to thank Miss Y. Masuda and Miss N. Shiomi for their assistance, and Miss T. Hirata for preparing the manuscript.

This work was supported by a grant-in-aid for scientific researches of the Ministry of Education.

References

- 1) C. P. Swann, C. E. Mandeville and W. D. Whitehead: *Phys. Rev.* **79** (1950) 598.
- 2) C. P. Browne: *Phys. Rev.* **95** (1954) 860.
- 3) P. M. Endt, J. C. Kluyver and C. Van der Leun: *Physica* **20** (1954) 1299.
- 4) R. W. Kavanagh, W. R. Mills and R. Sherr: *Phys. Rev.* **97** (1955) 248.
- 5) L. L. Green, J. J. Singh and J. C. Willmott: *Proc. Phys. Soc. London A*, **69** (1956) 335.
- 6) S. Hinds and R. Middleton: *Proc. Phys. Soc. London* **73** (1959) 501.
- 7) J. Muto, K. Okano and T. Tabata: Read before the spring meetings of the Physical Society of Japan (1959).
- 8) J. Muto and K. Okano: *Mem. Coll. of Sci., Univ. of Kyoto, A*, **28** (1958) 337.
- 9) R. Tangen: *K. Norske Vidensk. Selsk. Skr.* (1946).
- 10) W. E. Taylor, L. N. Russell and J. N. Cooper: *Phys. Rev.* **93** (1954) 1056.
- 11) J. C. Kluyver, C. Van der Leun and P. M. Endt: *Physica* **20** (1954) 1287.
- 12) S. E. Hunt and D. A. Hancock: *Phys. Rev.* **97** (1955) 567; *Proc. Phys. Soc. London A*, **67** (1954) 446.
- 13) E. A. Wolicki, R. Jastrow and F. Brooks: *Naval Research Laboratory, Report NRL-4833*, Washington, D.C. 1956.
- 14) P. M. Endt and C. M. Braams: *Rev. Mod. Phys.* **29** (1957) 683.
- 15) C. P. Browne: *Phys. Rev.* **114** (1959) 807; *Phys. Rev. Letters*, **2** (1959) 188.
- 16) M. T. Sharp, J. M. Kennedy, B. J. Sears and M. G. Hoyle: *Atomic Energy of Canada, Limited, Report AECL-97*, Chalk River, 1953.
- 17) J. R. Holt and T. N. Marsham: *Proc. Phys. Soc. London A*, **66** (1953) 258.
- 18) J. M. Ferguson: *Phys. Rev.* **112** (1958) 1238.
- 19) I. Taylor and F. de Barros (Manchester University): Private communication.
- 20) L. A. Radicati: *Phys. Rev.* **87** (1952) 521.
- 21) G. Morpurgo: *Phys. Rev.* **110** (1958) 721.
- 22) R. Thieberger and I. Talmi: *Phys. Rev.* **102** (1956) 923.

Gamma-rays from the Reaction $\text{Al}^{27}(p, \gamma)\text{Si}^{28}$

By Kotoyuki OKANO

Department of Physics, Faculty of Science, Kyoto University

(Received September 3, 1959)

Gamma-rays from the reaction $\text{Al}^{27}(p, \gamma)\text{Si}^{28}$ have been studied at the four resonances occurring at $E_p = 226, 294, 326$, and 405 keV by the use of a large NaI crystal scintillation spectrometer. The gamma-ray transitions from the resonance states to the levels in Si^{28} at 1.78 MeV(1st), 4.62 MeV(2nd), 6.91 MeV, and 8.58 MeV were observed. Spins and parities of these levels and some of the resonance levels are deduced from the anisotropies of gamma-rays as follows: 4.62 MeV, $J = 4^{(+)}$; 6.91 MeV, $J = 2^{\pm}$ or 4^+ ; 8.58 MeV, $J = 3^+$; 11.90 MeV, $J = 4^{(-)}$; 11.98 MeV, $J = 4^-$. $J = 4^{(+)}$ for the second excited state suggests the collective nature of this excited v level which has been expected from the other evidences found in neighbouring nuclei. The gamma-ray yield and the branching ratios of each resonance level are also given.

§ 1. Introduction

The reaction $\text{Al}^{27}(p, \gamma)\text{Si}^{28}$ shows numerous sharp resonances in the region below $E_p \sim 2$ MeV.¹⁾⁻⁴⁾ The gamma-ray spectrum was investigated by Casson at the 326 and 405 keV resonances,⁵⁾ and by Rutherglen *et al.* at the five resonances between $E_p = 400-700$ keV.⁶⁾ The latter authors also measured the angular distributions of the more prominent gamma-rays and assigned spins and parities to the resonance states and the first excited state in Si^{28} . In $E_p = 0.65-2.20$ MeV region, Gove *et al.* measured the angular distribution of gamma-ray transitions leading to the ground or first excited state.⁷⁾

The excitation energies of the first and second excited states in Si^{28} have been determined accurately by magnetic analyses of the charged particles from the reactions $\text{Si}^{28}(p, p')\text{Si}^{28}$ and $\text{P}^{31}(p, \alpha)\text{Si}^{28}$.^{8), 9)} The higher excited states were investigated by the reaction $\text{Al}^{27}(d, n)\text{Si}^{28}$ by Calvert *et al.*,¹⁰⁾ and by Rubin *et al.*¹¹⁾ The angular distribution of neutron groups from this reaction has also been measured, and the orbital angular momentum of a captured nucleon was assigned on the basis of the theory of the stripping reaction.^{10), 12)}

In the present work, the more complete investigation of the de-excitation gamma-rays following the proton capture in Al^{27} was attempted, and some definite informations were obtained. From the angular distribution of each gamma-ray line, spins and parities are assigned to some of the levels in Si^{28} includ-

ing the second excited state, which will be of some interest from the point that the collective mode of excitation may exist in this mass region.

§ 2. Experimental Apparatus and Procedure

A proton beam up to $70 \mu\text{A}$ from the 500 KV Cockcroft-Walton generator, after 90° magnetic deflection, passed through a hole of 8 mm diameter at a distance of 15 cm from the target, producing a beam spot of about 8 mm high and 4 mm wide on the target. A thick target of pure aluminium was used in order to permit high incident current, which is necessary for securing the reasonable counts at the weak resonances as observed. The proton current incident upon the target was measured by a current integrator of the Higinbotham type, and for the gamma-ray yield measurements, two pieces of permanent magnet were installed at the entrance of the target box, which itself served as a Faraday cage.

Gamma-ray spectra were measured with a large NaI(Tl) crystal, 5 in. in diameter by 4 in. thick, coupled to an EMI-6099B photomultiplier. Another 1.5 in. dia. $\times 2$ in. NaI(Tl) crystal, coupled to a Dumont-6292 photomultiplier, was used as a monitor counter and also for the coincidence measurements. These crystal-photomultiplier assemblies were shielded by a layer of lead, about 5 cm thick, and were mounted on a large angular distribution apparatus, as illustrated in Fig. 1 of the preceding paper. No collimation of the

gamma-ray beam was used. The output pulses from the photomultiplier were delay-line shaped, and fed into a 100-channel Hutchinson-Scarrott type or a 10-channel Johnstone type pulse height analyser. The counting loss due to the dead time of the 100-channel analyser was corrected by the discriminator-scaler system connected in parallel. In coincidence measurements, amplified pulses from the small crystal were pulse-height selected, by means of a single channel analyser, and phase-inverted, which opened the gate circuit of the 100-channel analyser, to whose main input were fed the 3.7μ sec-delayed pulses from the large crystal. The coincidence resolving time of the system (2τ) was about 6 microseconds.

The gamma-ray energies were determined by the 10-channel analyser, whose linearity and stability were superior to those of the 100-channel analyser. In these measurements, the crystal was placed close to the target (~ 30 mm), in order to increase the counting rate to a reasonable level. Energy calibration was carried out with the gamma-rays from the radioisotopes Na^{22} (1.277 Mev) and ThC'' (2.614 Mev) for the low energy part of the spectra, as well as with the gamma-rays from the reaction $F^{19}(p, \alpha, \gamma)O^{16}$ (6.14 Mev) and the reaction $Al^{27}(p, \gamma)Si^{28}$ (7.25–7.36 Mev) using the known Q -value of 11.588 Mev, for the high energy part of the spectra.

For coincidence measurements, two crystals were generally placed at 90° and 270° to the beam, respectively, and as close to the target as possible (~ 25 mm). Although this geometry was necessary to get a reasonable coincidence rate, sum peaks due to the coincident detection of cascade gamma-rays were expected to appear in both crystals to a significant amount, and these effects were corrected using the crystal efficiencies and the standard line shapes described below, taking into account the angular correlation of two gamma-rays.

To obtain the angular distribution of each gamma-ray line, it is necessary to subtract the escape peaks or the Compton tails of higher energy gamma-rays, i.e. to decompose the observed spectrum into the sum of various gamma-rays. For this purpose, the line shape of monochromatic gamma-rays emitted from a point source at a distance of 150 mm

from the front face of the crystal was measured as a function of energy with the following sources: $B^{11}(p, \gamma)C^{12}$ (11.67, 4.43 Mev), $C^{13}(p, \gamma)N^{14}$ (8.00 Mev), $F^{19}(p, \alpha, \gamma)O^{16}$ (6.14 Mev), Na^{24} (2.754 Mev), $C^{12}(p, \gamma)N^{13}$ (2.37 Mev), Na^{22} (1.277 Mev), Cs^{137} (0.662 Mev). The spectra of five of these for the large crystal are shown in Fig. 1. The monochromatic line shape of any desired energy can be constructed with the help of a special diagram, which allows easy interpolation between the measured monochromatic line shapes mentioned above.

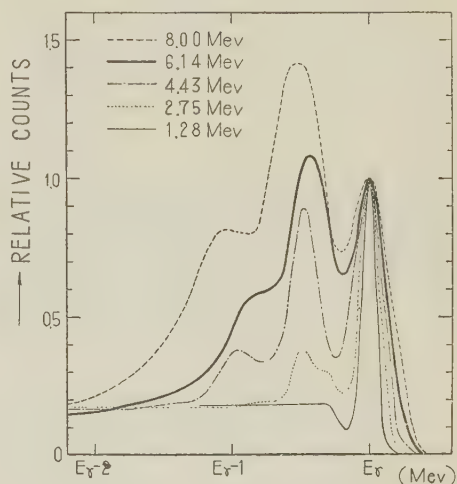


Fig. 1. Line shapes of monochromatic gamma-rays of five different energies for 5 in. dia. $\times$ 4 in. NaI crystal, with no collimation. The distance between the front face of the crystal and sources was 150mm.

The actual scintillation spectrum was decomposed into its constituent gamma-rays by successive numerical fitting and subtraction of the monochromatic line shapes thus obtained. Individual pulse height spectra of each component gamma-ray obtained by this process are shown by the dotted curves in Figs. 5–7, and these were used for the calculation of relative intensities as well as angular distributions. The relative intensities of each gamma-ray were computed from the decomposed spectra using the crystal detection efficiencies tabulated by Wolicki *et al.*¹³⁾ This method was checked to be correct within 10% with the cascade lines from the $B^{11}(p, \gamma)C^{12}$ reaction (11.67, 4.43 Mev) and from Na^{24} (2.75, 1.37 Mev). The quoted errors for the relative intensities (Tables I–IV) include this 10% uncertainty for the efficiency, as well as the statistical

uncertainty of the counts in the peak channels where the standard line shape was numerically normalized to fit the original spectra. In the evaluation of the angular distribution coefficient A_2 , we must take into account not only the statistical error, but the uncertainty due to the various possible errors in the subtraction process but this was found not to exceed the statistical error by the trial of analysing and combining several data, and the quoted error for A_2 in Tables III and IV are mainly of statistical origin.

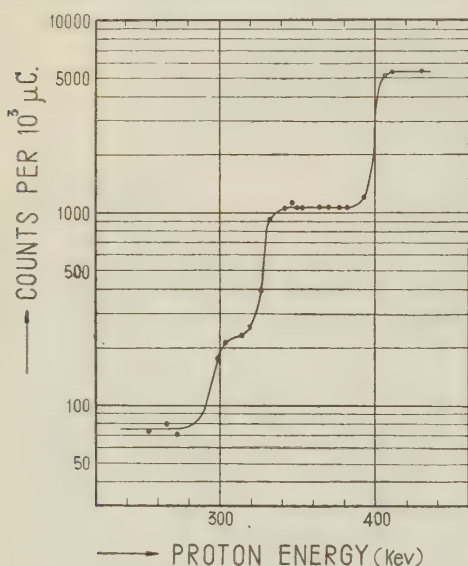


Fig. 2. Thick target excitation curve of gamma-rays observed at 55 degrees to the proton beam, with the discriminator bias corresponding to the gamma-ray energies greater than 5.8 Mev. The distance between the front face of the crystal and the target was 29mm.

In angular distribution measurements, the front face of the crystal was 150 mm apart from the target, and the integrated proton current was used as a monitor as well as the 10-channel counts from the other small NaI crystal, placed about 80 mm apart from the target. The distance between the centre of the target and the main crystal was held constant within one millimeter with a jig at any angular setting of the counter, and if the deviation of the proton beam spot from the centre of the target was recognized, the correction was applied. The gamma-ray spectra were measured just above and below a resonance, and the contributions from the lower resonances were subtracted as well as the

background of various kinds. This subtraction was safely performed in virtue of the fact that the contributions from the lower resonances are always small in our E_p region, as can be seen from the thick target excitation curve shown in Fig. 2, and also of the fact that the gamma-rays from the 294, 326, and 405 kev resonances have almost the same spectra and angular distributions.

Background of various sources was found to appear, i.e. natural radioactivity and cosmic-ray with a constant level, reaction gamma-rays produced by the proton beam striking the magnet box, defining slits, and aperture, whose intensities depend on the energy as well as on the intensity of the proton beam, and also contaminant gamma-rays from the target such as the 2.3 Mev gamma-ray from the $C^{12}(p, \gamma)N^{13}$ reaction and the 6.14 Mev gamma-ray from the $F^{19}(p, \alpha, \gamma)O^{16}$ reaction, which are due to a slow buildup of carbon and fluorine on the target surface.

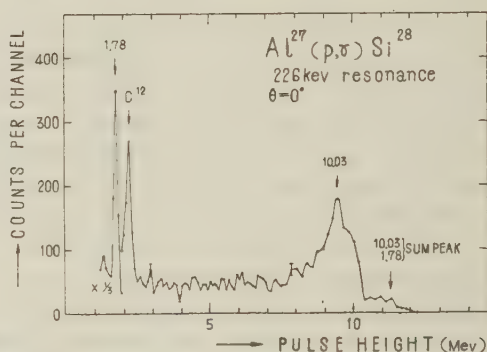


Fig. 3. Scintillation spectrum taken at the 226-kev resonance at zero degree to the proton beam with the front face of the crystal close to the target (~ 30 mm).

Although a liquid air cold trap was installed in front of the target box, these contaminant gamma-rays could not be eliminated altogether, and frequently appeared as a contaminant peak, which was very troublesome. Considerable portions of these backgrounds however, could be subtracted by the above-mentioned process.

§ 3. The Decay Scheme of the De-excitation Gamma-rays

In Figs. 3-7 are shown the gamma-ray spectra observed at the resonances of 226, 294, 326, and 405 kev proton energy. The

226 keV resonance level, at an excitation of 11.80 MeV in Si^{28} , decays predominantly to the first excited state at 1.78 MeV, while other three resonance levels decay mainly to the second excited state at 4.62 MeV and the state at 6.91 MeV, by the gamma-rays of 7.25–7.36 MeV and 4.96–5.07 MeV, respectively. At the 405 keV resonance, weak transition to the first excited state is also present, in accordance with the observation of Rutherglen *et al.*⁶⁾ The state at 6.91 MeV

Table I. Gamma-rays observed at the 226 keV resonance.

E_γ (MeV)	Transition	Relative intensity
10.03 ^a	11.81→1.78	100±10.8
1.78	1.78→0	94.2± 9.9
	11.81→4.62	<7.8
	11.81→6.91	<4.7
2.19	C^{12} contamination	

a: Energy standard.

Table II. Gamma-rays observed at the 294 keV resonance.

E_γ (MeV)	Transition	Relative intensity
7.25 ^a (6.80) ^b	11.87→4.62 8.58→1.78	72.5±7.8
5.14±0.05 4.98±0.05	6.91→1.78 11.87→6.91	39.0±5.1
4.08±0.10	(11.87→7.90)	8.0±3.8
3.29±0.04	11.87→8.58	10.1±2.1
2.85±0.03	4.62→1.78	56.4±6.7
1.77 ₅ ±0.015	1.78→0	
6.14	{(F ¹⁹ contamination) (7.90→1.78) 4.62→0	<1.1
3.8	existence doubtful	4.7±3.3
2.22	C^{12} contamination	

a: Energy standard

b: Not direct observation.

decays by a 5.13 ± 0.04 MeV gamma-ray to the first excited state, so the peak at about 5.1 MeV is actually composed of two components. This is verified by the coincidence spectra gated by the 7.3 MeV peak and by this 5 MeV peak as shown in Fig. 9, and in addition, by a slight energy shift of one component recognized at the 294 and 326 keV resonances. Our 6.91 ± 0.03 MeV state is considered to correspond to the 6.88 ± 0.06 MeV state observed by Rubin *et al.* by the

$Al^{27}(d,n)Si^{28}$ reaction.¹¹⁾ The 4.62 MeV state fed from the resonance level by the 7.3 MeV line, decays predominantly to the first excited state by a 2.84 MeV gamma-ray. The direct ground state transition was found to be less than 2% of cascade transition.

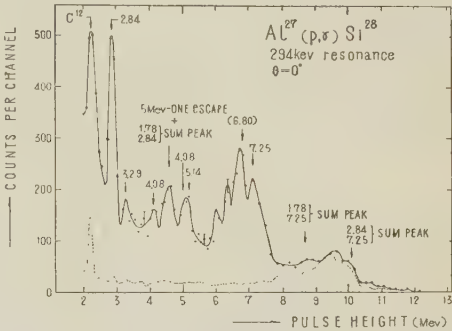


Table III. Gamma-rays observed at the 326 keV resonance.

E_γ (MeV)	Transition	Relative intensity	Anisotropy A_2
7.29 ± 0.10 (6.80) ^b	$11.90 \rightarrow 4.62$ $8.58 \rightarrow 1.78$	75.7 ± 7.6	0.26 ± 0.03
5.13 ± 0.05 4.99 ± 0.05	$6.91 \rightarrow 1.78$ $11.90 \rightarrow 6.91$	32.7 ± 4.6	0.23 ± 0.07
3.95 ± 0.10	$(11.90 \rightarrow 7.90)$	7.9 ± 2.6	
3.33 ± 0.04	$11.90 \rightarrow 8.58$	5.4 ± 2.2	
2.84 ± 0.03 1.79 ± 0.015	$4.62 \rightarrow 1.78$ $1.78 \rightarrow 0$	83.4 ± 9.2	0.24 ± 0.04
8.4	existence doubtful		
6.14	$\left\{ \begin{array}{l} \text{F}^{19} \text{ contamination} \\ (7.90 \rightarrow 1.78) \end{array} \right.$		
	$4.62 \rightarrow 0$	< 1.6	
2.26	C ¹² contamination		

b: Not direct observation

326 keV resonance, and 3.40 ± 0.03 MeV at the 405 keV resonance. So this must be the primary gamma-ray de-exciting the resonance level to the state at 8.58 ± 0.04 MeV, observed by Rubin *et al.* as 8.57 ± 0.08 MeV. This 3 MeV component is in coincidence with the 7.3 MeV peak at the 405 keV resonance, but not with the pulses corresponding to the energy region 8 to 9 MeV, as can be seen in

Fig. 9. As the decomposition of the 7.3 MeV peak at the 405 keV resonance is consistent with the presence of a 6.8 MeV component of about 10% of the main component, the 8.58 MeV level must decay to the first excited state by a gamma-ray of 6.80 MeV energy.

A 4.60 MeV gamma-ray was observed at the 405 keV resonance with the intensity of about 10% of that of the 2.84 MeV component, in the singles spectra. At the 294 and 326 keV resonances, however, it is less than 2%, if present. In the coincidence spectrum at the 405 keV resonance gated by the 7.3 MeV peak, the 4.60 MeV component is less than 3% of 2.84 MeV line, after careful subtraction of the sum peak due to the coincident detection of the 2.84 and 1.78 MeV cascade gamma-rays. Since the other evidences are reported that the 4.6 MeV gamma-ray observed in the $\text{Al}^{27}(p, \gamma)\text{Si}^{28}$ reaction is not due to the direct ground state transition from the 4.62 MeV level,¹⁴⁾ we assigned it tentatively as a transition from the 9.2₂ MeV $T=1$ level to the 4.62 MeV second excited level. The transition from the resonance level to this 9.2 MeV level includes 2.7₆ MeV gamma-ray, which would be difficult to observe in our case, if it is present, on account of the strong 2.84 MeV line.

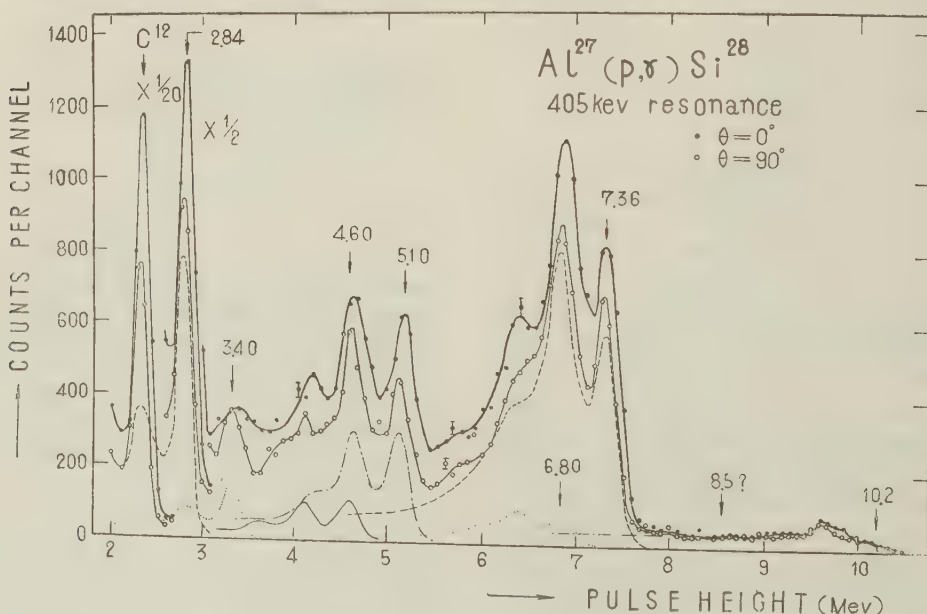


Fig. 6. High energy part of the scintillation spectra taken at the 405 keV resonance at zero and 90 degrees to the proton beam. Contributions from the lower resonances were subtracted and the dotted curves show the individual pulse height spectra into which the 90 degrees spectrum was decomposed.

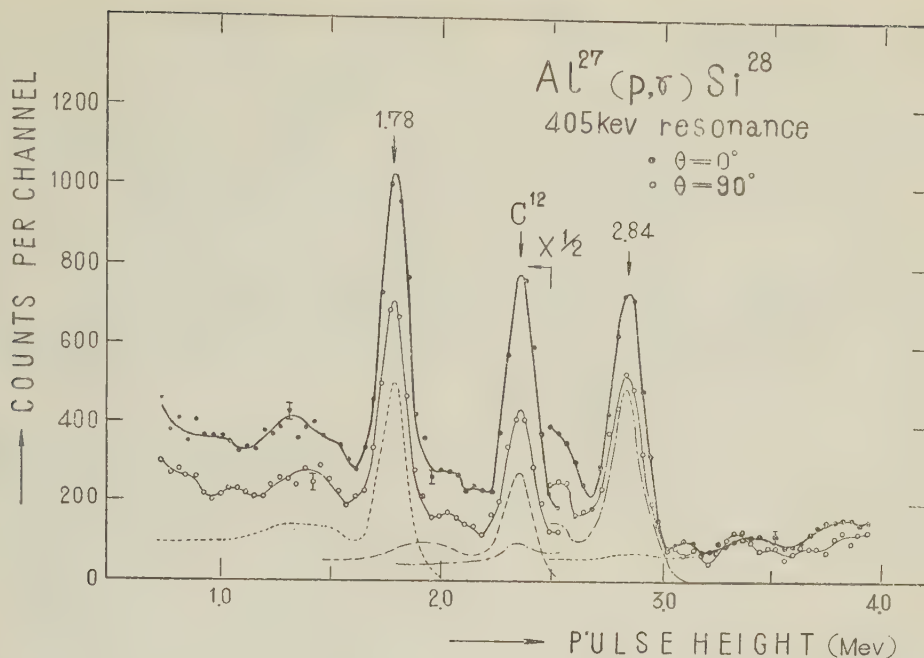


Fig. 7. Low energy part of the scintillation spectra at the 405 keV resonance, taken at zero and 90 degrees to the proton beam. Contributions from the lower resonances were subtracted. The dotted curves show the individual pulse height spectra into which the 90 degrees spectrum was decomposed.

A gamma-ray of about 4 Mev energy was present at the 294 and 326 keV resonances, as listed in Tables II and III, but the yield was too low to make a definite coincidence work on these weak components at these resonances, and only a tentative assignment is that it may be the transition from the resonance level to the 7.90 Mev level known from the (d, n) reaction, with a possible decay of the 7.90 Mev level to the first excited state by a 6.12 Mev gamma-ray. The 6.12 Mev component was difficult to discriminate against the possible background 6.14 Mev gamma-ray from the $F^{19}(p, \alpha, \gamma)O^{16}$ reaction,

and its existence was not established. Also a slight indication of the presence of about 8.5 Mev gamma-ray was observed, but its existence or the decay mode could not be established with any certainty. The decay scheme thus determined is illustrated in Fig. 10 together with the branching ratios of each resonance level, and the excitation energies deduced from the gamma-ray energies are

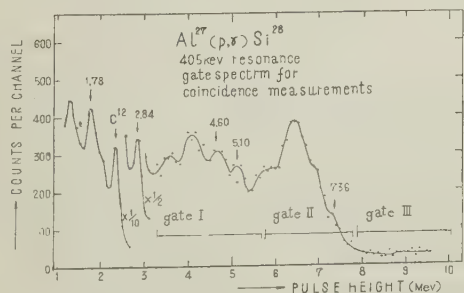


Fig. 8. Small-crystal scintillation spectrum, taken at the 405 keV resonance. Gate positions for the coincidence measurements are shown.

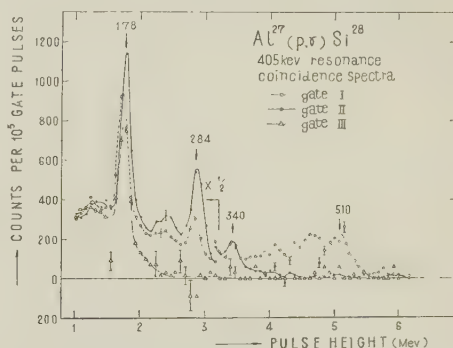


Fig. 9. Coincidence spectra taken at the 405 keV resonance, with a thick target and a 100-channel pulse height analyser. Small contributions from chance coincidence counts, sum peak counts in the large crystal, and false coincidence counts due to the sum peaks in the gate crystal were carefully subtracted.

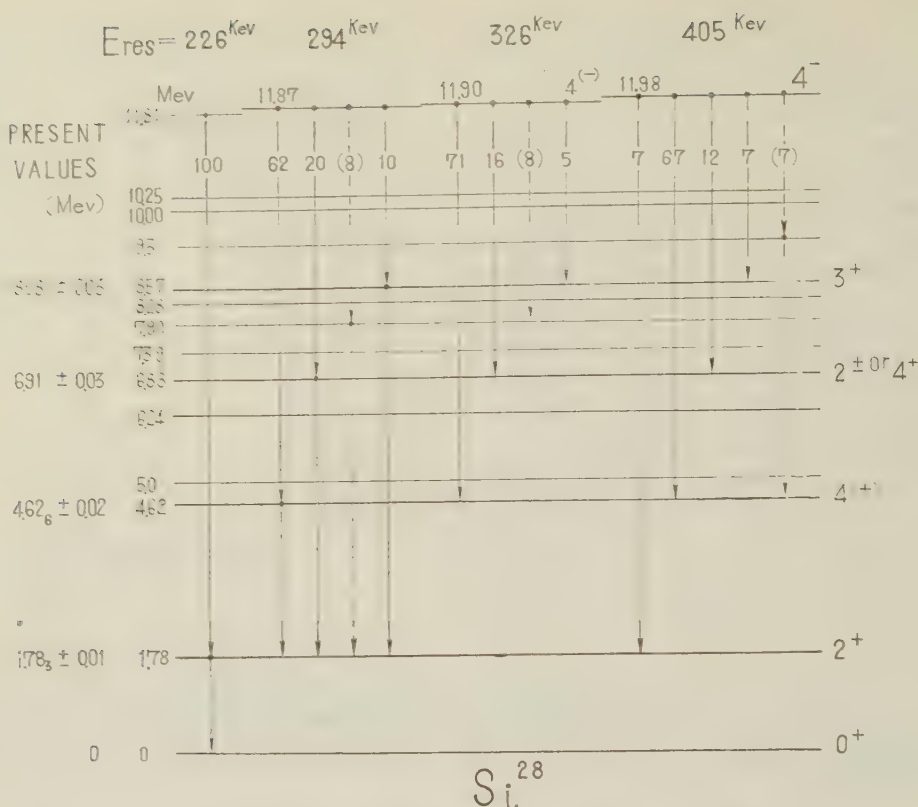


Fig. 10. Level scheme of Si^{28} . The levels above 5 Mev excitation are mainly those obtained by the $\text{Al}^{27}(d, n)\text{Si}^{28}$ reaction. The spin assignment of the 4.62, 6.91, 8.58, 11.90, and 11.98-Mev levels are discussed in the text. The assignment for the first excited state is from previous work.

compared with the other values reported previously.^{(8), (9), (11)} In Tables I to IV are summarized the gamma-ray energies and relative intensities at each resonance, together with the anisotropies of each gamma-ray line, where measured. The relative intensities are shown as the number of photons per 100 captures.

It will be of some value to compare the present result with those previously reported. Rutherglen *et al.* interpreted the 7.3 Mev peak of their gamma-ray spectra as a mixture of two components, of transitions from the resonance level to the levels at 4.6 and 5.2 Mev, with such a comparable intensity ratio as to affect the angular distribution appreciably.⁽⁶⁾ Present work with better resolution is inconsistent with this interpretation. Monoenergetic line shape for a 7.3 Mev gamma-ray, interpolated from the line shapes of monochromatic 6.14 and 8.00 Mev gamma-ray, and shown by the dotted lines in Figs. 5 and 6, is in close agreement with the line shapes

observed in the $\text{Al}^{27}(p, \gamma)\text{Si}^{28}$ reaction. Only a small amount of 6.8 Mev component is considered to be included in this peak, which was confirmed by the coincidence results. Also, the de-excitation gamma-ray of the 5.2 Mev level, i.e. a 3.4 Mev line of fixed energy or a 5.2 Mev line coincident with the 7.3 Mev peak, is to be found with the Rutherglen's scheme, but there was not any appreciable indication of its presence.

The 5.1 Mev gamma-ray had been assigned as a cascade transition decaying from the resonance level through the level at 7.1 Mev to the first excited state.⁽⁹⁾ Though the decay mode was confirmed by our coincidence results, precise determination of gamma-ray energies indicates that the intermediate state is at 6.91 ± 0.03 Mev excitation. This value, as stated above, is in agreement with the excitation energy of the corresponding level, 6.88 ± 0.06 Mev, obtained from the energy measurement of neutron group in the reaction $\text{Al}^{27}(d, n)\text{Si}^{28}$, within experimental error.

As to the direct ground state transition from the second excited state, though a 4.6 Mev line was observed and reported at the 993 kev resonance, it was found that the line is not accompanied by the 2.84 Mev–1.78 Mev cascade gamma-rays at the other resonances nor in the reaction $Mg^{26}(\alpha, n, \gamma)Si^{28, 13), 16)}$ Rutherglen *et al.* also do not report 4.6 Mev line at the five resonances between $E_p = 400$ –700 kev. These are in agreement with our results, and are consistent with the $J=4^{(+)}$ assignment to the 4.62 Mev level as described below.

§ 4. Spin and Parity Assignments to Levels in Si^{28}

The angular distribution of each gamma-ray line was measured by analysing spectra taken at zero and 90 degrees to the proton beam. The anisotropy observed was fitted into the angular distribution formula $W'(\theta) = 1 + G_2 A_2 P_2(\cos \theta)$, where G_2 , the correction factor for finite solid angle of the detector, was calculated to be 0.916 between $E_\gamma = 3 \sim 8$ Mev for our geometry.* In Tables III and IV are given the measured values of A_2 for each gamma-ray, at the 326 and 405 kev resonances. The resonances at 226 and 294 kev were too weak to allow any definite conclusions to be

* In the case of a d -wave capture followed by a quadrupole or higher multipole transition, the angular distribution formula includes $P_4(\cos \theta)$ term, i.e.

$$W'(\theta) = 1 + G_2 A_2 P_2(\cos \theta) + G_4 A_4 P_4(\cos \theta).$$

We have measured only the anisotropy, $R = W'(0^\circ)/W'(90^\circ)$, on the assumption that the d -wave capture followed by a quadrupole transition will be a rather rare case in our E_p region. The anisotropy R is related to the coefficients A_2 in the absence of the $P_4(\cos \theta)$ term by the relation

$$R = (1 + G_2 A_2) / \{1 - (G_2 A_2 / 2)\}$$

i.e. $A_2 = (R - 1) / G_2 (1 + R/2)$, which was used throughout the analysis, and to the coefficients A_2, A_4 by the relation

$$R = (1 + G_2 A_2 + G_4 A_4) / \{1 - (G_2 A_2 / 2) + (3G_4 A_4 / 8)\}$$

if the $P_4(\cos \theta)$ term is present. Therefore, the experimentally obtained A_2 value, $(R - 1) / G_2 (1 + R/2)$, deduced on the assumption of the absence of $P_4(\cos \theta)$ term, is to be compared with the theoretical value $\{A_2 + (5G_4 A_4 / 12G_2)\} / \{1 + (7G_4 A_4 / 12)\}$ in the case the $P_4(\cos \theta)$ term is expected. As we had no exact value for G_4 , we used instead the theoretical value $\{A_2 + (5A_4 / 12)\} / \{1 + (7A_4 / 12)\}$, but the difference from the exact value was estimated to be only a few percents.

drawn from measurements.

When a resonance state is well isolated and is formed by a single angular momentum of the incident proton, as in our cases, the theoretical angular distribution of the primary or the intermediate gamma-ray in the (p, γ) cascade is uniquely determined by specifying the quantum numbers and parameters such as channel spin s , orbital angular momentum l of the incident proton, spin J_1, J_2 , etc. of the intermediate states (see Fig. 11), spin I of the state to which the observed gamma-ray leads, and the multipole order L_1, L'_1, L_2, L'_2 , etc. and mixing ratios δ_1, δ_2 , etc. of the intermediate gamma-ray as well as the observed gamma-ray.** As the ground state spin of

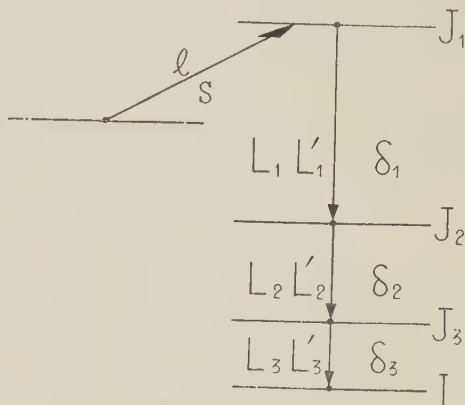


Fig. 11. Energy level diagram for the $(p, \gamma, \gamma, \gamma)$ reaction showing the notation employed in the text for quantum numbers.

** In the case that the resonance level is well isolated and the interference between the incident proton waves does not occur, the theoretical angular distribution formulae for the first, second, and third gamma-rays in the (p, γ) cascade are expressed as follows, apart from trivial and complicated factors involving powers of -1 ,

1st gamma-ray:

$$W(\theta) = \sum_k Z(lJ_1 lJ_1, sk) Z_1(L_1 J_1 L'_1 J_1, J_2 k) P_k(\cos \theta)$$

2nd gamma-ray:

$$W(\theta) = \sum_k Z(lJ_1 lJ_1, sk) \times W(J_1 J_2 J_1 J_2, L_1 k) Z_1(L_2 J_2 L'_2 J_2, J_3 k) P_k(\cos \theta)$$

3rd gamma-ray:

$$W(\theta) = \sum_k Z(lJ_1 lJ_1, sk) W(J_1 J_2 J_1 J_2, L_1 k) \times W(J_2 J_3 J_2 J_3, L_2 k) Z_1(L_3 J_3 L'_3 J_3, I k) P_k(\cos \theta).$$

The components of different channel spin or different multipole order of the preceding radiations contribute incoherently. In our analysis, numerical values of the functions Z, W , and Z_1 , and the sign of multipole interference term which affects the sign of δ_1 and δ_2 cited in Table VI, were taken from reference 16.

Table IV. Gamma-rays observed at the 405 kev resonance.

E_γ (Mev)	Transition	Relative intensity	Anisotropy A_2
10.2±0.15	11.98→1.78	6.6±2.3	
7.36 ^a	11.98→4.62	66.5±6.7	0.21±0.02
6.80	8.58→1.78	(7.2±1.4) ^b	
5.10±0.04	{ 11.98→6.91 6.91→1.78	24.4±2.9	0.25±0.05
4.60±0.05	(9.22→4.62)	7.5±2.5	
3.40±0.03	11.98→8.58	7.2±1.4	-0.16±0.08
2.84±0.02	4.62→1.78	76.6±7.7	0.24±0.02
1.785±0.015	1.78→0	106.4±13.8	0.25±0.03
8.5	existence doubtful		
	4.62→0	<2.3	
2.34	C ¹² contamination		

a: Energy standard
b: Not direct observation

Table V. Anisotropies A_2 computed for pure radiation.

			Theoretical A_2 for the first gamma-ray leading to the state of spin			
l	J_1	s	$J_2=2$	$J_2=3$	$J_2=4$	$J_2=5$
0	2 ⁺ or 3 ⁺	2 or 3	isotropic			
1	1 ⁻	2	-0.010	0.014	—	—
	2 ⁻	2	-0.350	0.100	-0.143	—
	2 ⁻	3	0.100	-0.029	0.041	—
	3 ⁻	2	-0.240	0.300	-0.100	0.143
	3 ⁻	3	0.300	-0.375	0.125	-0.179
	4 ⁻	3	0.281	-0.196	0.275	-0.100
	0 ⁺	2	isotropic			
	1 ⁺	2	0.050	-0.071	—	—
	1 ⁺	3	-0.014	0.020	—	—
	2 ⁺	2 or 3	s -wave ($l=0$) predominant			
2	3 ⁺	2 or 3				
	4 ⁺	2	0.373 ^a	-0.281	0.393	-0.143
	4 ⁺	3	0.134 ^a	-0.028	0.039	-0.014
	5 ⁺	3	—	0.334	-0.248	0.374

a: Coefficient of $P_4(\cos \theta)$ appears in these cases, and the value $\left(A_2 + \frac{5}{12} A_4\right) / \left(1 + \frac{7}{12} A_4\right)$ is listed, which is to be compared with the experimental anisotropies.

Al^{27} is $J=5/2$, with even parity, the resonance states that can be formed by s -, p -, or d -wave proton capture are as follows: s -wave, $l=0$, $J_1=2^+, 3^+$; p -wave, $l=1$, $J_1=1^-, 2^-, 3^-, 4^-$; d -wave, $l=2$, $J_1=0^+, 1^+, 2^+, 3^+, 4^+, 5^+$. The theoretical angular distribution coefficients of the primary gamma-ray de-exciting the re-

sonance state are given in Table V, for all these possible cases, with the combination of channel spin $s=2$ or 3, and the final state spin $J_2(=I$ in this case) $=2, 3, 4$, or 5 .¹⁶⁾ Here the coefficients are calculated assuming the pure multipolarity of the allowed lowest order, but in the actual cases, it is necessary to take into account a small admixture of higher multipole component, and the coefficients as a function of mixing ratio δ_1 , were calculated for the cases as cited in Table VI, which are of actual interest. Angular distribution measurements of the second and third gamma-rays in the cascade are also necessary in order to determine the spin sequence uniquely, and the theoretical coefficients of these cascade gamma-rays, which contain the parameters such as the channel spin mixing ratio t and the multipole mixing ratios of the first and second gamma-rays, δ_1 and δ_2 , were also calculated.

405 kev resonance :

The main transition at this resonance is the 7.36 Mev—2.84 Mev—1.78 Mev triple cascade. From the measured A_2 values of these three lines, we can deduce spin and parity of the resonance state as well as the second excited state.

The observed anisotropy of the 7.3 Mev peak is $A_2=0.21\pm0.02$, in fair agreement with the result obtained previously, $A_2=0.19\pm0.007$.⁶⁾ The effect of a small admixture of the 6.8 Mev component which is included in this peak was corrected assuming the 8.58 Mev level as $J=3^+$ (as discussed below), and using the theoretical angular distribution coefficient for the second transition of a $4^-(E1)3^+(M1)2^+$ cascade, $A_2=-0.196$. The corrected value, $A_2^{\text{exp. corr.}}=0.24\pm0.02$, was adopted for the 7.36 Mev component. The observed anisotropy of the second gamma-ray, 2.84 Mev line, is $A_2=0.24\pm0.02$. Even if the 2.76 Mev line, proposed as a possible transition from the resonance level to the 9.2 Mev (3^+) level, would exist, the correction due to the effect of this line was estimated to be $+0.01$ or less. The observed anisotropy of the third gamma-ray, 1.78 Mev line, is $A_2=0.25\pm0.03$. The effect of the contribution from other two cascades, namely, 3.40 Mev—6.80 Mev—1.78 Mev and 5.07 Mev—5.13 Mev—1.78 Mev must be corrected. If we take the 6.91 Mev level, the intermediate level of the

Table VI. Comparison between the experimentally observed anisotropies and the theoretical predictions, for the main triple cascade transition at the 405 kev resonance.

Spin sequence $J_1(I_1L_1')J_2(L_2L_2')\cdot$ $J_3(L_3L_3')I$	First gamma-ray $A_2^{exp.} = 0.24 \pm 0.02$	Second gamma-ray $A_2^{exp.} = 0.24 \pm 0.02$	Third gamma-ray $A_2^{exp.} = 0.26 \pm 0.03$ Expected values
$2^-(DQ)2(DQ)2^+(Q)0^+$	No; $A_2^{theor.} < 0.195$ ($t = \infty$) ^a	No; $A_2^{theor.} < 0.06$	No 0.012
$2^-(DQ)3(DQ)2^+(Q)0^+$	Yes; if $0.11 < \delta_1 < 0.15$ ($t = 0$) ^a	Yes; if $-0.02 < \delta_2 < 0.02$ $3.7 < \delta_2 < 4.3$	No $-0.340 \sim -0.337$ $-0.102 \sim -0.097$
$3^-(DQ)2(DQ)2^+(Q)0^+$	Yes; if $5.8 < t < 12.5$ ^{b,c}	Yes; if $0.73 < \delta_2 < 1.1$ $2.2 < \delta_2 < 4.7$	No $-0.094 \sim -0.034$ $0.029 \sim 0.068$
$3^-(DQ)3(DQ)2^+(Q)0^+$	Yes; if $0.06 < t < 0.14$ ^c	Yes; if $-0.68 < \delta_2 < -0.49$ $-4.7 < \delta_2 < -2.7$	No $0.159 \sim 0.171$ $0.052 \sim 0.077$
$3^-(DQ)4(Q)2^+(Q)0^+$	Yes; if $0.07 < \delta_1 < 0.11$ ($t = \infty$) ^a	No; $A_2^{theor.} = -0.350 \pm 0.006$	No $-0.350 \sim -0.349$
$4^-(QO)2(DQ)2^+(Q)0^+$	Yes; if $-0.09 < \delta_1 < -0.03$	Yes; if $-0.13 < \delta_2 < -0.04$ $-2.0 < \delta_2 < -1.6$	No $0.136 \sim 0.140$ $-0.020 \sim 0.004$
$4^-(DQ)3(DQ)2^+(Q)0^+$	unfavourable; $0.37 < \delta_1 < 0.43$	Yes; if $-0.48 < \delta_2 < -0.42$ $-6.3 < \delta_2 < -4.7$	Yes $0.226 \sim 0.237$ $0.070 \sim 0.076$
$4^-(DQ)4(Q)2^+(Q)0^+$	Yes; if $-0.13 < \delta_1 < -0.03$	Yes; $A_2^{theor.} = 0.238 \pm 0.006$	Yes $0.237 \sim 0.239$
$4^+(Q)2(DQ)2^+(Q)0^+$	Yes; if $0.90 < t < 1.79$	Yes; if $-0.42 < \delta_2 < -0.14$ $-1.70 < \delta_2 < -1.0$	No $0.014 \sim 0.058$ $-0.010 \sim 0.009$
$4^+(DQ)4(Q)2^+(Q)0^+$	Yes; if $0.60 < t < 0.95$ ^c	Yes; $A_2^{theor.} = 0.221 \pm 0.014$	Yes $0.215 \sim 0.241$

- a: Unique channel spin was assumed for these cases as the mixing of other channel spin requires larger values of δ in the interpretation of our results.
- b: t is the fraction of states formed by the channel spin $s=3$ to the states formed by $s=2$.
- c: As δ_1 is considered to be small, δ_1 was taken to be zero for these cases. Non zero value of δ_1 allows larger range for channel spin ratio t , but it does not affect the following conclusions.

latter cascade, as $J=2\pm$, $A_2^{exp.corr.}$ is 0.26_4 and if we take it as $J=4^+$, $A_2^{exp.corr.}$ remains 0.25. Therefore, the correction is not serious in either case, and we adopted the value $A_2^{exp.corr.} = 0.26 \pm 0.03$ for the third gamma-ray of the triple cascade.

From the anisotropy of the first gamma-ray, ten spin sequences listed in Table VI seem to be possible with reference to Table V, and the calculated theoretical angular distribution coefficients of the first gamma-ray for these cases, taking into account the multipole mixing, are compared with the experimentally obtained values in Table VI. Here, the ground and first excited states are known to be $J=0^+$ and 2^+ , respectively. As is shown in Table VI, eight cases of ten can be fitted with the experimental anisotropy of the first gamma-ray with the appropriate values for the channel spin mixing ratio t or multipole mixing δ_1 . One case is unfavourable because quadrupole component is too large. The experimental anisotropy of the second gamma-ray was compared with the theoretical values which were obtained by applying the values of t or δ_1 determined

from the anisotropy of the first gamma-ray to the original formulae for the second gamma-ray, which contain t , δ_1 , and δ_2 , in general. Two cases can be fitted without any specification, and again six cases can be fitted with the appropriate choices of the mixing ratio, δ_2 , as shown in the third column of Table VI. In the last column of Table VI, the theoretically expected coefficients for the third gamma-ray are given which were calculated using the values of t , δ_1 and δ_2 , previously determined. Here the selection is rather stringent, as no multipole mixing can occur in this last gamma-ray, and after all, only the two cases, i.e. $4^-(DQ)4(Q)2^+(Q)0^+$ and $4^+(DQ)4(Q)2^+(Q)0^+$, are found to be consistent with our observation. There may seem to remain a slight possibility in the sequence $4^-(DQ)3(DQ)2^+(Q)0^+$ from our data, but this is further depressed by the fact that the angular distribution of the gamma-ray(s) leading to the level at about 4.6 Mev from the 652 kev resonance, measured by Rutherglen *et al.*,⁶⁾ is also very different from the distribution expected with the pure dipole transition to a $J_2=3$ level, rather agreeing with

the distribution expected with the assignment of $J_2=4$. Thus the $J=4$ character for the second excited state is considered to be well established. The parity of the state is expected to be even, but this point will further be discussed later. As to the resonance state, $J_1=4^-$ assignment will be reasonable, since no alpha-particles from the $\text{Al}^{27}(p, \alpha)\text{Mg}^{24}$ reaction was observed at this resonance⁶⁾ and also our A_2 coefficients for the second and third gamma-rays seem to favour the $4^-(DQ)4(Q)2^+(Q)0^+$ sequence. This assignment is in accord with that of Rutherglen *et al.*, based upon the gamma-ray decay modes and the absence of alpha-particles. The main transition at this resonance, 7.36 Mev gamma-ray to the second excited state, is therefore of $E1$ character, with a small ($\sim 1\%$) admixture of $M2$ component. Fairly significant transition to the 2^+ first excited state from the resonance state must also be of $M2$ (or $M2+E3$) character, and the $M2$ mixture in the main $E1$ component is considered to be quite possible.

From the anisotropy of $A_2=0.25\pm 0.05$ for the composite 5.1 Mev line, the intermediate state at 6.91 Mev is found to be consistent with $J_2=2$ or 4, as is seen from Table VI, now that the resonance state was determined to be $J_1=4^-$. $J_2=3^+$ or 3^- is excluded, since in this case, above A_2 coefficient cannot be fitted with the theoretical value in a reasonable range of δ_1 or δ_2 . If the parity of the state is odd, as is consistent with the assignment of $l_p=1$ to the stripping pattern of the (d, n) neutron group leading to this state,¹²⁾ $J_2=2^-$ may be decisive as the level decays to the 2^+ first excited state. But the possibility of $J_2=2^+$ or 4^+ cannot be excluded, since the $l_p=1$ assignment is not well established.

The 8.58 Mev level had been assigned to be $J=2^+$ or 3^+ on the basis of the $l_p=0$ pattern of the neutron group leading to this level.¹²⁾ Then, $A_2=-0.16\pm 0.08$ of our 3.40 Mev line, decaying from the 4^- resonance state to this level, fixes the spin and parity to be 3^+ .

326 kev resonance:

At this resonance, gamma-ray angular distributions and decay modes are almost the same as those at the 405 kev resonance, and the A_2 values of the first and second gamma-

rays in the main cascade fix the resonance state to be $J_1=4^+$ or 4^+ , as can be seen from Table V and Table VI. P -wave capture is favourable from the gamma-ray yield which is noted in the next section.

§ 5. Gamma-ray Yields and Proton Widths

From the thick target yield of gamma-rays de-exciting the resonance level, the quantity $(2J_1+1)\Gamma_p\Gamma_\gamma/(\Gamma_p+\Gamma_\gamma)$ was calculated for the four resonances and is listed in Table VII. In this calculation, the efficiency of the counter was taken from the tables of Wolicki *et al.*,¹⁴⁾ applying it to our decomposed spectra, and the stopping power of Al was taken from the experiments by Warshaw.¹⁷⁾ The absolute values of our results are smaller by about a factor of two than the previous measurements using a G-M counter,³⁾ to whose efficiency may be ascribed some part of the discrepancy, as the precise gamma-ray spectra had been unknown. As is clear from Table VII, the gamma-ray yield decreases rapidly with the proton energy, and this is considered to be due to the influence of the Coulomb barrier. The limiting factor of the resonance strength $\Gamma_p\Gamma_\gamma/(\Gamma_p+\Gamma_\gamma)$ must, therefore, be Γ_p , and we are forced to assume $\Gamma_p \ll \Gamma_\gamma$, in our resonances. The proton widths Γ_p , obtained with this assumption, are listed in the fourth column of Table VII. At the resonances above $E_p \sim 600$ kev, resonance strengths do not increase with the energy on the average, indicating that they are limited by Γ_γ . The magnitude of radiation widths, deduced from the resonance strengths at this region, are about 0.1~1 ev, as are also generally found in neighbouring nuclei. Our values of Γ_p listed are smaller by about two orders of magnitude than these normal widths for Γ_γ , and the above assumption, $\Gamma_p \ll \Gamma_\gamma$, is considered to be valid. To remove the influence of the Coulomb barrier, the square of the reduced width γ_p was calculated using the graphs of Coulomb wave functions,¹⁸⁾ and the results are shown in Table VII, in unit of the sum rule limit, $\hbar^2/\mu R^2$. Here μ is the reduced proton mass, $AM_p/(A+1)$, and the channel radius R was taken as $R=1.5A^{1/3} \times 10^{-13}$ cm. The resulting reduced widths are nearly constant, indicating that the decrease of the resonance strength can almost be explained by a barrier factor. If we assume d -wave capture

Table VII. Resonance strenghts and proton widths.

Resonance energy (kev)	$(2J_1+1) \Gamma_p \Gamma_\gamma / (\Gamma_p + \Gamma_\gamma)$ (ev)	J_1	Γ_p (ev)	Incident proton orb. ang. momentum	$\gamma_p^2 / (\hbar^2 / \mu R^2)$
405	0.15 ± 0.03	4	0.017	1	3.3×10^{-3}
326	0.028 ± 0.006	4	0.0031	1	6.0 "
294	0.0042 ± 0.0013	4^a	0.00047	1	3.1 "
226	0.00094 ± 0.0003	2^b	0.00019	0	6.7 "

a: At this resonance, 7.25 Mev gamma-ray was anisotropic with a positive A_2 value, suggesting $J_1=4\pm$ or 3^- . As the transition to the 2^+ first excited state was not found, we assumed tentatively as $J_1=4$. $J_1=4^+$ assignment with a d -wave capture leads to $\gamma_p^2 / (\hbar^2 / \mu R^2) \approx 70 \times 10^{-3}$.

b: The 226 kev resonance state decays almost completely to the 2^+ first excited state, and the 10 Mev de-excitation gamma-ray was measured to be nearly isotropic. So $J_1=1^-$, $2^\pm$, or $3^\pm$ may be possible. From the absence of the transition to the 4^+ state, we assumed tentatively as $J_1=2$.

for the 326 kev resonance, γ_p^2 amounts to $120 \times 10^{-3} (\hbar^2 / \mu R^2)$, 12 percent of the sum rule limit. Therefore $J=4^-$ assignment to the resonance state with a p -wave capture is preferable. As to the 226 kev resonance, p -wave assignment gives $\gamma_p^2 \approx 32 \times 10^{-3} (\hbar^2 / \mu R^2)$, while s -wave assignment, consistent with the nearly isotropic distribution of the gamma-radiation, gives a value nearly equal to those obtained at the three higher resonances. But a definite assignment can not be given, since a considerable fluctuation may be expected for γ_p^2 . In Weisskopf's estimate of $\gamma_p^2 = D / \pi K R$,¹⁹⁾ if the values of $K \sim 10^{13}$ cm and $D \sim 200$ kev, a plausible level distance in our case, are assumed, we have $\gamma_p^2 / (\hbar^2 / \mu R^2) = (D / \pi K R) / (\hbar^2 / \mu R^2) \sim 7 \times 10^{-3}$, rather in good agreement with our experimental results.

§ 6. Discussions

From the results of our work and those of previous workers, many resonance levels in the $Al^{27}(p, \gamma)Si^{28}$ reaction were found to decay mainly to the ground state, first excited state, second excited state, or the 6.91 Mev excited state, with different relative intensities from resonance to resonance. De-excitations to some other levels also exist, but they are weak and limited in number. Second excited state at 4.62 Mev was found to decay through the first excited state to the ground state.

Recently it was found that the nuclei in the $18 < A < 30$ region are expected to have large deformation and the strong coupling collective model may be applicable to a description of the level structure of these nuclei.^{20), 21), 22)} This was suggested from the fact that the

level sequences and other properties of the mirror pair, $Mg^{26}-Al^{25}$, well investigated by means of (p, γ) and (d, p) reactions, were successfully described in terms of the rotational model.^{20), 23)} Applications to other nuclei in this region were also tried by several authors, and Bromley *et al.* explained the level properties of Si^{29} in the frame of this model.²⁴⁾ According to this interpretation, the core nucleus, Si^{28} , is expected to have deformations of $|\delta| \sim 0.2$, the value deduced from the equilibrium deformation using the Nilsson model, and the rotational excitations characterized by a $J=0^+, 2^+, 4^+, \dots$ spin sequence are expected. Since the second excited state of Si^{28} was determined to be $J=4$ from our results, this rotational description is considered to have some relevance to this nucleus. The parity of the second excited state must be even in this interpretation, of course.

One objection to this assignment is that Rubin adopted $l_p=1$ to fit the stripping pattern of the neutron group leading to the state at about 4.6 Mev in the $Al^{27}(d, n)Si^{28}$ reaction. Consequent odd parity second excited state was explained as a possible 2^- state, which can be expected, using a spheroidal potential shell model, from the combination of one particle in the $d_{5/2}(5/2)$ state and another in the $f_{7/2}(1/2)$ state, the configuration which makes available a low excited state of odd parity if we assume large positive deformation of the nucleus. This configuration, however, cannot make available a state of spin 4, and also there are some evidences that the Si^{28} may have negative spheroidicity.²⁴⁾ Furthermore, in a preceding experiment, Calvert *et al.* had not assigned

any definite l_p -value to the corresponding group, and also Rubin's $l_p=1$ assignment to his stripping pattern seems to be not free from some ambiguity. Therefore, we believe even parity for the 4.62 Mev second excited state, a plausible assignment from the various theoretical considerations.

There may seem to be some relevance for a vibrational description of the level structure to this nucleus, since on a pure $j-j$ coupling scheme, Si^{28} corresponds to the closing of the $d_{5/2}$ shell for both protons and neutrons, and therefore, spherical shape is expected to be preferred, in which case collective nature manifests itself as a vibrational oscillations of the nuclear shape. In this model, rather closely spaced triplet of $J=0^+, 2^+$, and 4^+ or a doublet of $J=2^+$ and 4^+ are expected as second excited states,²⁶⁾ which have not been found, however, in Si^{28} . High resolution work on the reaction $\text{P}^{31}(p, \alpha)\text{Si}^{28}$ indicates only a single level at an excitation of 4.617 ± 0.008 Mev, at the same position deduced from our gamma-ray energy measurements, 4.626 ± 0.020 Mev. No transition to the 2^+ member of this triplet was present in our resonance, nor was there any indication of an $l_p=0$ stripping pattern of the (d, n) neutron group leading to the state at about 4.6 Mev. Although the ratio of the excitation energy, $E_2/E_1=2.60$, may seem to favour the vibrational interpretation, introduction of a vibration-rotation correction term allows the interpretation in terms of a rotational excitation, with reasonable values for moment of inertia and vibrational quantum energy, as was shown by Bromley *et al.*²⁴⁾ Further measurements on this and other neighbouring nuclides, especially with high resolution and by various reactions, are necessary in order to establish the suitable model of the nucleus for this mass region.

Acknowledgments

The author wishes to thank Prof. K. Kimura for his interest and encouragement during the course of this work. He expresses his sincere thanks to Prof. J. Muto for his invaluable guidances and co-operative contributions to this work, and to Mr. T. Tabata for his co-operative efforts and patient aid in carrying out this investigation. He also wishes to thank Dr. T. Hayashi for helpful

discussions, Mr. H. Ogata for his contributions to the preparation of electronic equipments, and Mr. H. Hukuda for his assistance in the experiment. This work was supported financially by a grant-in-aid for scientific researches of the Ministry of Education.

References

- 1) R. Tangen: K. Norske Vidensk. Selsk. Skr. (1946).
- 2) S. E. Hunt and W. M. Jones: Phys. Rev. **89** (1953) 1283.
- 3) K. J. Broström, T. Huus and R. Tangen: Phys. Rev. **71** (1947) 661.
- 4) F. C. Shoemaker, J. E. Faulkner, G. M. B. Bouricius, S. G. Kaufmann and F. P. Mooring: Phys. Rev. **83** (1951) 1011.
- 5) H. Casson: Phys. Rev. **89** (1953) 809.
- 6) J. G. Rutherglen, P. J. Grant, F. C. Flack and W. M. Deuchars: Proc. Phys. Soc. London A, **67** (1954) 101.
- 7) H. E. Gove, E. B. Paul, G. A. Bartholomew and A. E. Litherland: Phys. Rev. **94** (1954) 749(A).
- 8) C. P. Browne, S. F. Zimmerman and W. W. Buechner: Phys. Rev. **96** (1954) 725.
- 9) P. M. Endt and C. H. Paris: Phys. Rev. **106** (1957) 764.
- 10) J. M. Calvert, A. A. Yaffe, A. E. Litherland and E. E. Maslin: Proc. Phys. Soc. London A, **68** (1955) 1008.
- 11) A. G. Rubin, F. Ajzenberg-Selove and H. Mark: Phys. Rev. **104** (1956) 727.
- 12) A. G. Rubin: Phys. Rev. **108** (1957) 62.
- 13) E. A. Wolicki, R. Jastrow and F. Books: Naval Research Laboratory, Report NRL-4833 (Washington D. C., 1956).
- 14) H. E. Gove: Nuclear Data Card. (1957) NRC 57-6-44. Si^{28} 57 # 5.
- 15) P. M. Endt and C. M. Braams: Rev. Mod. Phys. **29** (1957) 683.
- 16) W. T. Sharp, J. M. Kennedy, B. J. Sears, and M. G. Hoyle: Atomic Energy of Canada, Limited, Report AECL-97 (Chalk River, 1953).
- 17) S. D. Warshaw: Phys. Rev. **76** (1949) 1759.
- 18) W. T. Sharp, H. E. Gove and E. B. Paul: Atomic Energy of Canada, Limited, Report AECL-268 (Chalk River, 1953).
- 19) J. M. Blatt and V. F. Weisskopf: *Theoretical Nuclear Physics* (Jhon Wiley and Sons, New York, 1952) chap. VIII.
- 20) A. E. Litherland, E. B. Paul, G. A. Bartholomew and H. E. Gove: Phys. Rev. **102** (1956) 208.
- 21) E. B. Paul: Phil. Mag. **2** (1957) 311.
- 22) G. Rakavy: Nucl. Phys. **4** (1957) 375.
- 23) A. E. Litherland, H. McManus, E. B. Paul,

- D. A. Bromley and H. E. Gove: *Canad. J. Phys.* **36** (1958) 378.
 24) D. A. Bromley, H. E. Gove and A. E. Litherland: *Canad. J. Phys.* **35** (1957) 1057.
 25) L. Wilets and M. Jean: *Phys. Rev.* **102** (1956) 788.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 1, JANUARY, 1960

A 160 cm Synchro- and Variable Energy Ordinary Cyclotron

By Seishi KIKUCHI, Itaru NONAKA, Hiroshi IKEDA, Hiroo KUMAGAI,
 Yoshio SAJI, Junpei SANADA, Shigeki SUWA, Akira ISOYA, Izuo
 HAYASHI, Kazuhisa MATSUDA, Hisashi YAMAGUCHI, Takashi
 MIKUMO, Keigo NISHIMURA, Takashi KARASAWA,
 Shinsaku KOBAYASHI, Ken KIKUCHI, Satoru
 ITO*, Arata SUZUKI, Seiichiro TAKEUCHI**,
 and Hiroshi OGAWA

Institute for Nuclear Study, University of Tokyo
Tanashi-Machi, Kitatama-Gun, Tokyo

(Received September 4, 1959)

A 160 cm cyclotron have been constructed as the first accelerator of the Institute for Nuclear Study, University of Tokyo. This cyclotron can be used as a variable energy ordinary cyclotron as well as a synchro-cyclotron by changing the dee-system and the oscillator system.

As an ordinary cyclotron it can produce protons of any desired energy between 7.5 and 15 MeV, deuterons between 15 and 21 MeV, and α particles between 30 and 42 MeV. These beams are now being used for various experiments on nuclear reactions and for production of radioisotopes.

As a synchro-cyclotron, it can produce protons of 57 MeV in energy and the beam is extracted with high efficiency at a radius near $n = 1$ with an electrostatic deflector.

§ 1. Introduction

The Institute for Nuclear Study, University of Tokyo, has been founded in 1955 after two year's period for planning, and the facilities in the institute are open to the common usage by all the research members in Japan. A 160 cm synchro-cyclotron has been established as the first accelerator of this institute and the most remarkable characteristic of this cyclotron is that it can be used as an ordinary cyclotron as well as a synchro-cyclotron.

This accelerator, as an ordinary cyclotron, produces protons of any desired energy between 7.5 and 15 MeV, deuterons between 15 and 21 MeV and α -particles between 30 and

42 MeV. These accelerated particles are used for study of nuclear reactions or production of radioisotopes. As a synchro-cyclotron, it can produce protons of 57 MeV which can be used for study of characteristic nuclear reactions in this energy range. The general arrangement of the cyclotron and particle analysing apparatus are shown in Fig. 1. Key points of the design by which the two kinds of operation of a cyclotron were realized are shown in Fig. 2 (a) and (b). As can be seen in the figures, the electro magnet, the vacuum tank and the vacuum pump are common, and the oscillator system is interchanged for the two kinds of operation. The magnitude of magnetic field must be changed in two cases from several tenth of Wb/m² to 1.6 Wb/m², and we can perform this variation by changing

* Deceased.

** Now at Tokyo-Shibaura Electric Co., Ltd., Kawasaki, Kanagawa-ken.

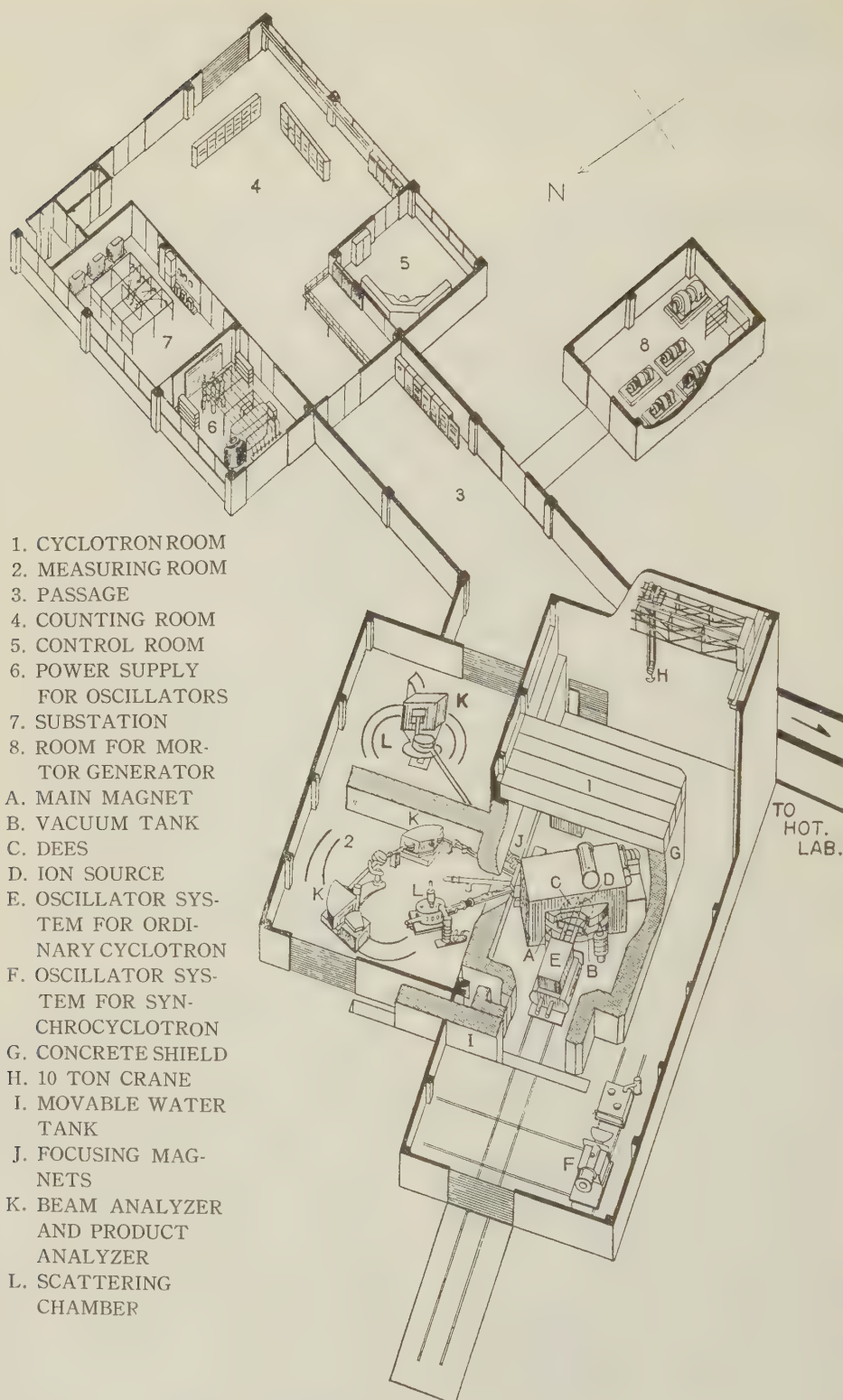


Fig. 1. General arrangement of the equipments.

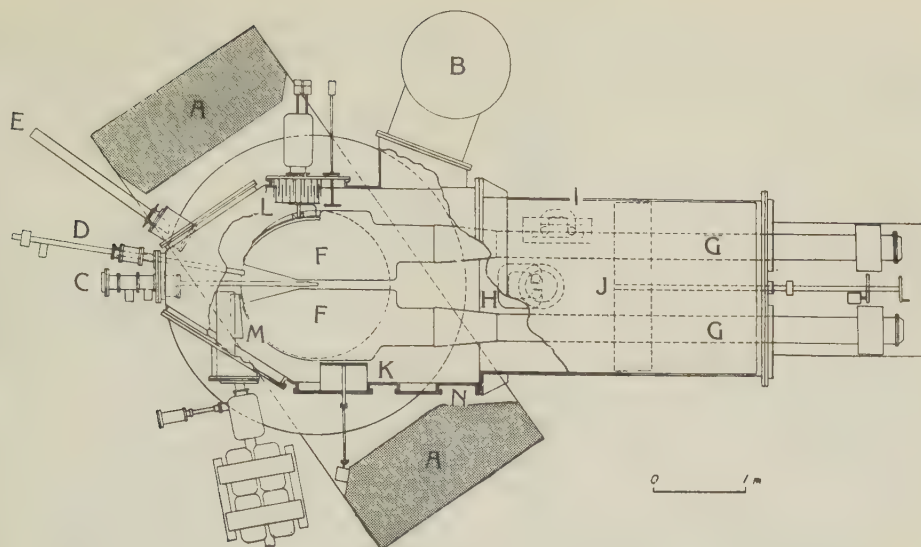


Fig. 2(a). Arrangement for the case of ordinary cyclotron.

- | | |
|---|--------------------------------|
| A: Magnet yoke, | B: 32 inch oil diffusion pump, |
| C: Ion source, | D: Current probe, |
| E: Target for radioisotope production, | |
| F: Dee | G: Stem, |
| H: Plate loop, | I: Cathode loop, |
| J: Shorting plate, | K: Capacity compensator, |
| L: $r-f$ deflector, | M: Magnetic channel, |
| N: Common flange for both oscillator systems. | |

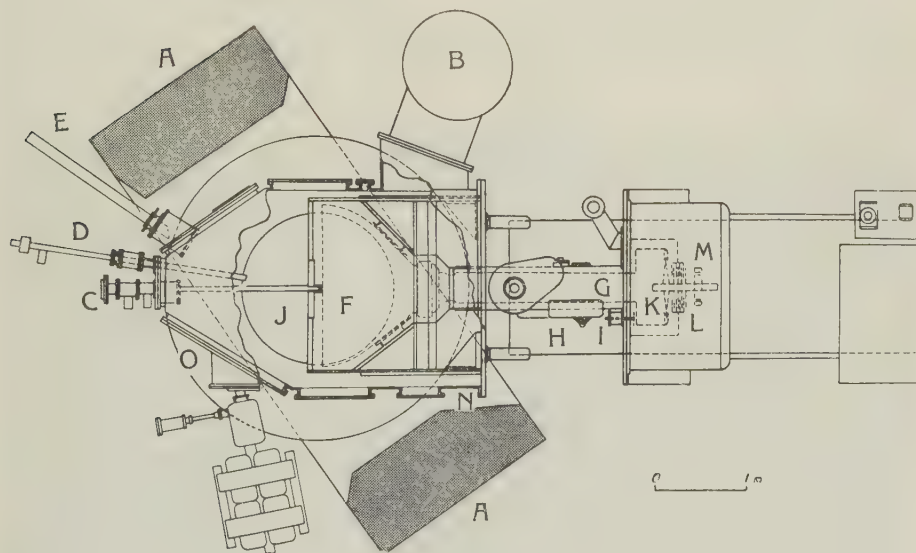


Fig. 2(b). Arrangement for the case of synchro-cyclotron,

- | | |
|---|--------------------------------|
| A: Magnet yoke, | B: 32 inch oil diffusion pump, |
| C: Ion source, | D: Current probe, |
| E: Target for radioisotope production, | |
| F: Dee, | G: Stem, |
| H: Plate loop, | I: Cathode loop, |
| J: Dummy dee, | K: Rotating condenser, |
| L: By pass condenser, | M: Induction motor, |
| N: Common flange for both oscillator systems, | |
| O: Exit port for the synchro-cyclotron beam. | |

Table I. Specifications and performances

(1) Main magnet			
Total Weight	70 tons		
Weight of copper	21.8 tons		
Number of turns of coils	1536		
Maximum current	400 A		
Pole diameter	160 cm (63 inches)		
Pole tip gap	25 cm		
Magnetic induction at gap	0–1.96 Wb/m ²		
Field stability	±10 ⁻⁴ over all excitation		
M. G. set	240 kW		
(2) Vacuum system			
Main diffusion pump	32'' dia., speed 20000 1/sec		
Fore diffusion pumps	10'' dia., two in series		
Rotary pump	Speed 3000 1/min		
End vacuum	1 × 10 ⁻⁶ mm Hg		
Operating vacuum	5–8 × 10 ⁻⁶ mm Hg		
(3) Oscillator			
(a) For ordinary cyclotron			
Resonant cavity	Shielded Lecher-wire type, λ/4 mode		
Frequency	Variable between 8.4 and 12.0 Mc/sec		
Q of the cavity	4500–5000 (obs.)		
Capacity of each dee	360 pF (calc.)		
Oscillator type	Grounded grid, self-excited, cathode at high voltage		
D. C. bias	Up to 1500 V, negative		
Oscillator tube	Two 9T71 (RCA 5770 equiv.) in parallel.		
	Maximum plate dissipation, 50 kW × 2		
Power Supply	250 kW, 6-pole mercury arc rectifier, D. C. voltage range, 2 to 15 kV		
(b) For synchro-cyclotron			
Resonant cavity	12.8Ω coaxial type, λ/2 mode		
Frequency	Modulated between 24.3 and 20.3 Mc/sec		
Q of the cavity	~1000		
Capacity of dee	550 pF		
Rotating condenser	Gap between plate, 1 mm		
	Maximum capacity, 830 pF		
	Minimum capacity, 130 pF		
Modulation frequency	Up to 2250 c/sec		
Oscillator type	Grounded grid, self-excited, cathode at high voltage		
D. C. bias	Up to 1500 V, negative		
Oscillator tube	Single 8T50,		
	Maximum plate dissipation, 25 kW		
Power supply	Common with that for ordinary cyclotron		
(4) Performances			
(a) Ordinary cyclotron			
Particles	Range of energy	Internal beam (stable)	External beam (stable)
Proton	7.5–15 MeV	600 μA	200 μA*, 0.5 μA**
Deuteron	15–21 MeV	600 μA	200 μA*, 0.5 μA**
α-particle	30–42 MeV	300 μA	100 μA*, 0.3 μA**
(b) Synchro cyclotron			
Particles	Energy	Internal beam	External beam
Proton	57 MeV	0.8 μA (at n=1.0)	0.5 μA***

* On the current probe, about 10 cm away from the exit of the deflector.

** At the Faraday cup of the scattering chamber, after passing through two collimating slits each 5 mm in diameter and 80 cm apart.

*** At the exit port of the vacuum tank of the cyclotron.

only the coil current of the magnet without any change of so called "shimming", as described in § 3.

As this cyclotron is for common usage by research members who have wide field of researches, it has been designed so as to have an above mentioned wide range of ability. For the same reason, the details of this cyclotron have been designed to acquire a reliable and stable working conditions.

Another important characteristic feature of this cyclotron is that the energy of the beam is variable when it is operated as an ordinary cyclotron. The variation of the beam energy is achieved by changing the magnetic field and the frequency of the oscillator, instead of the method of energy absorption by foils.

Such a variable energy cyclotron must full-fill the following two conditions.

(a) The main magnet must be able to produce variable magnetic field adequate for cyclotron, including the focussing ability, by only changing the coil current, that is, without any change of the shimming on the surface of the pole tip.

(b) The frequency of the oscillator can be changed easily.

To fullfill the first condition (a), the pole profile of the magnet is designed so that the

magnetic induction in the pole is constant. This is the same method as the design principle of the magnet of the 16'' variable energy cyclotron at Institute for Solid State Physics, University of Tokyo¹⁾. To fulfill the second condition (b), the resonator of the oscillator is a shielded Lecher-wire type and special cautions are payed in the design of the shorting plate so as to be moved very easily.

In the synchro-cyclotron case, this accelerator has the following special feature that 80% of the accelerated ions can pass over the $n=0.2$ point and can reach to $n=1$ point. About 50% of the internal beam can be extracted with an electrostatic deflector just before $n=1$ point, as will be described in a separate paper. The origins by which such an extraction method has succeeded are the very good azymuthal uniformity of the magnetic field, low value of the dee bias voltage and selected configuration of the ion source and feeler. All these may have served to supress the radial oscillations and vertical diverging of ions.

The progress of the design and manufacturing was as follows.

1953 Discussion on fundamental qualifications was started.

July, 1954 Fundamental qualifications were

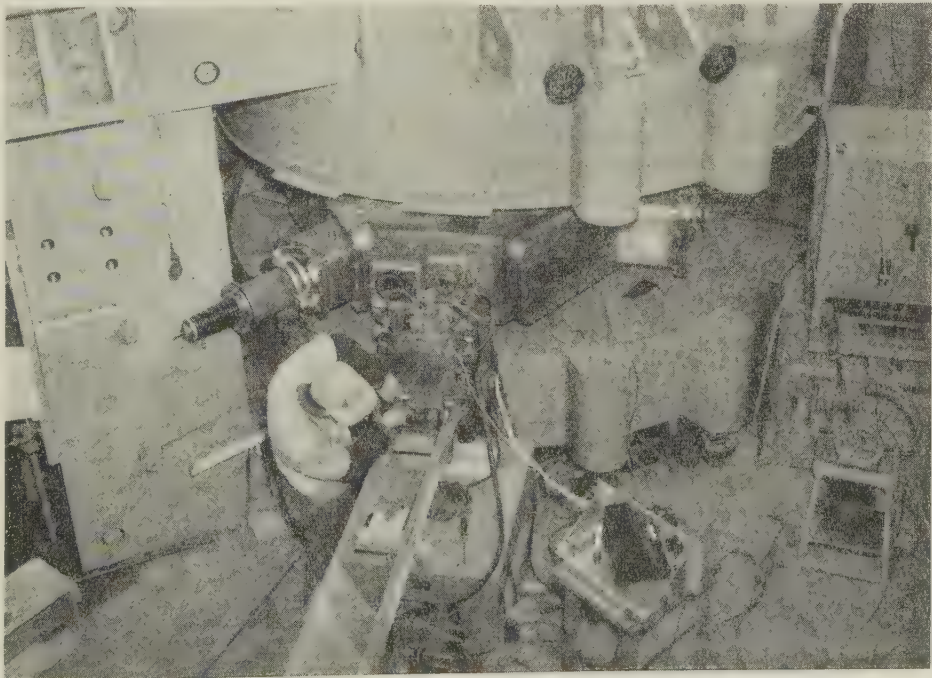


Fig. 3. Cyclotron at the stage of assembling, seen from the side of the ion source.

fixed, and design was started.

Feb. 1955 Design for the order to manufacturers was finished, and ordered to Tokyo-Shibaura Electric Co. Ltd.

Sept. 1957 Finished as an ordinary cyclotron.

May, 1958 Finished as a synchro-cyclotron.

Specifications and performances are shown in Table I.

§ 2. General Arrangements of the Equipments

Most equipments are arranged on the earth's surface, since the Institute is located on an open field and the level of subterranean water is high. The median plane of the magnetic field is 120 cm high from the floor, and the base of the main magnet and the oil diffusion pumps are set in a pit. Fig. 1 shows the general arrangement of the equipments. Fig. 3 is a photograph of the cyclotron taken from the side of the ion source.

The cyclotron is shielded by concrete on the three sides and top, and by movable water tank on the west side. A CO₂ fire extinguisher system is provided in this cave. The alarm rings when the temperature rises to the dangerous level. Either of the two oscillator systems which is not being used is placed at the south-west corner of the cyclotron room. It is covered by a vacuum can and the accelerating electrodes are maintained in vacuum. The crossed rails are used when the oscillator systems are exchanged each other.

The extracted beams from the cyclotron are lead to the next room through beam ducts and are focused on the target by focusing magnets. All the motor generator sets for magnet excitation are assembled together in a separated room because of their vibrations and noises. The hot laboratory at the south is connected by a passage to the cyclotron building.

§ 3. Main Magnet

In order to achieve the dual purpose of a synchro- and ordinary-cyclotron and the energy variation of the ordinary cyclotron, the magnet is required to have such a property that its radial field distribution varies as small as possible in a wide range of flux density. This requirement is fulfilled by adopting the special design of the pole piece whose profile is

shown in Fig. 4. Its feature is that the diameter increases considerably from the pole tip to the pole base. Consequently, the magnetic induction becomes nearly constant in the pole piece and the saturation of the iron near the edge of the pole tip is carefully avoided. The effects of this design are seen in the excitation curve and the radial field distribution, both of which are shown in Fig. 5. The excitation curve does not show any saturation effect until the flux density reaches to a considerably high value, and the field distribution shows only small variation in a wide range of flux density.

The raw material of the yokes and the pole pieces is ordinary soft-steel of carbon content less than 0.2%. The pole pieces and the yokes consist of 10 blocks, each of which are

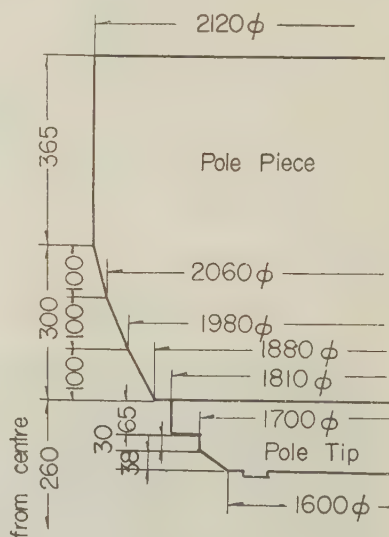


Fig. 4.

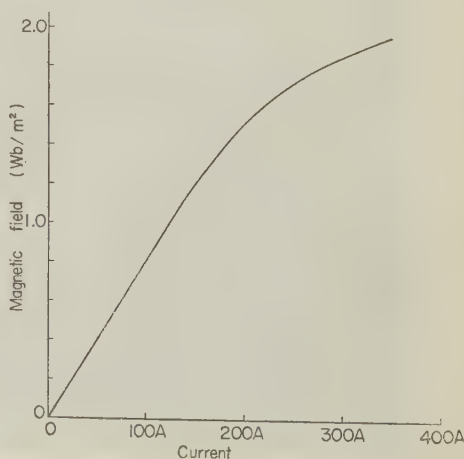


Fig. 5(a).

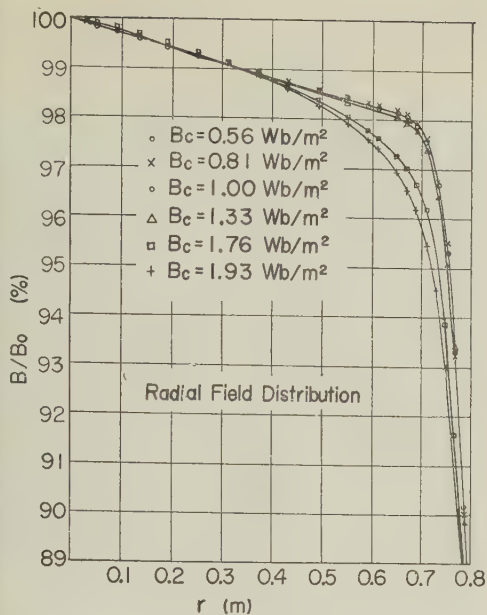


Fig. 5(b). Radial field distribution of the main magnet.

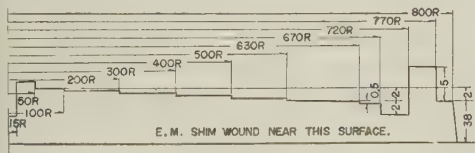


Fig. 5(c). Cross section of the pole tip of the main magnet.

made of rolled iron plates about 100 mm thick. The pole tips are 135 mm thick and have Rose shim on them, but have no shim gaps. The coils are housed in steel tanks and are cooled by circulation of transformer oil. The coil current is stabilized by a single feed-back loop of a chopper amplifier. The cross section of the pole tip is shown in Fig. 5(c). The pole face is shaped conically in step wise. This cone shape gives a field fall-off about 2% at the exit radius and provides the magnetic focusing action for the beam. The shape of Rose shim has been determined by a cut-and-try method in view of the small variation of field distribution in a wide range of flux density. The variation as shown in Fig. 5 is tolerable for the various aims of the cyclotron. This magnet has also “Electromagnetic Shims”. There are some grooves on the rear surfaces of the pole tips in which circular coils and coils of sector shape are wound. We can change azimuthal and radial field distributions slightly by this electromagnetic shims

during the operation of the cyclotron. However, fortunately there is no need for us to use these shims at least in the case of ordinary cyclotron.

As regards the azimuthal asymmetry of the field, the first harmonics has the most important effect to the beam orbit. The width of the pole gap had a small first order asymmetry when the magnet was constructed, and the results of field measurements also showed a similar symmetry. This was corrected by inserting a thin steel liner at the appropriate position between the upper and the side yoke. Thus the amplitude of the first harmonics of field asymmetry becomes less than 1/10000 over all range of excitation. The location of the magnetic median plane and the measurement of n -value of the field are performed by a new method. Its principle is such that the radial component of field is measured carefully with a search coil whose effective axis coincides exactly to the geometrical centre plane and with a electronic flux meter. The results show such deviations of the magnetic median plane from the geometrical centre plane as less than 5 mm near the centre and less than 1mm near the exit radius. The n -values of field are shown in Fig. 6. The further details of the magnet and of the field measurements were described elsewhere.²⁾

§ 4. Vacuum Tank and Components Attached to It.

(i) Vacuum Tank

The vacuum tank is made of 18-8 stainless

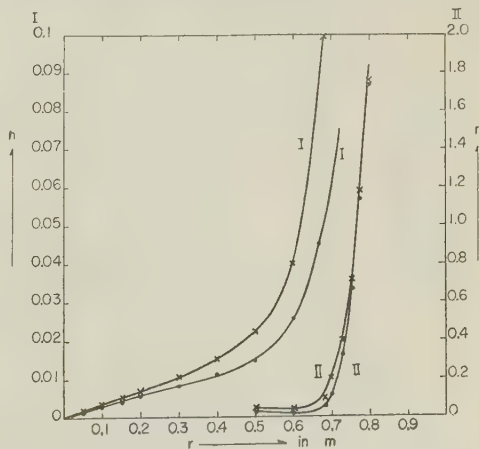


Fig. 6. n -values of magnetic field of the main magnet.

× $B_c = 1.76 \text{ wb/m}^2$
 • $B_c = 1.33 \text{ wb/m}^2$

steel. The walls are 2 cm thick and welded together. The rather large length along the supporting rod of the ion source is required by the conditions to be fulfilled by the combined use for ordinary cyclotron and synchro-cyclotron.

The top and the bottom walls are bolted to the pole tip of the main magnet. A band of "O" ring is provided on the vertical surface of the pole tip. No vacuum difficulties have been encountered. The inner surfaces of tank walls and pole tip have linings of copper plates of 4 mm thick to allow the radio-frequency current to flow. On the side walls of the vacuum tank, many ports are provided such as the beam exits of ordinary cyclotron and of synchro-cyclotron, the connection port to the vacuum pump, the inlet of ion source rod, current probe, target and so on.

(ii) Ion Source and Feelers

The ion source consists of a graphite anode and a hair pin type tungsten filament of 2 mm in diameter. The anode is of Oak Ridge type³⁾ for ordinary cyclotron and open cone for synchro-cyclotron.

The filament is heated by D.C. obtained from a three-phase full wave rectifier with germanium rectifiers. Its maximum output is 5 volts and 400 amperes. The D.C. power supply of the anode is a three-phase full wave rectifier with selenium rectifiers and its maximum output is 500 volts and 5 amperes.

The life of tungsten filament exceeds 30 hours. In the occasion of its exchange, we need not break the vacuum of cyclotron by using a gate valve, and also need not remove

all the connections of electric leads and water cooling pipes, because they are made flexible. The exchange finishes within 10 minutes.

The feeler for ordinary cyclotron is a vertical feeler of graphite which is attached to the edge of the north dee and shown in Fig. 7. The cone of ion source supports another graphite plate along the dee line. Such a set of two plates has a function of selecting the interval of the initial phase of ions relative to the radio frequency voltage. And accordingly, we can suppress the ion load for the oscillator power and obtain the more mono-energetic beams with the good grouping of orbit centres. We have compared it with the ordinary feelers of jaw type and recognized the effects above described. The feelers for synchro-cyclotron are the jaws of graphite attached to the edges of dee. The details of them are shown in Fig. 19 (§ 14).

(iii) Deflector

The deflector described in this section is for ordinary cyclotron. It is an r-f type external deflector which can be superimposed by a negative D.C. potential up to 50 kV. An r-f by-pass capacitor of 600 pF is mounted on the supporting rod of the deflector in vacuum. All components are attached to a flanged plate which has wheels and can be moved easily for mounting and removing.

Exit radius is designed to be 72 cm. Deflector channel begins at 90° counter clockwise from the dee line and extends for 60° of arc. The distance between deflector and septum is 9 mm at the entrance of deflector channel and 15 mm at the exit. The septum is made of graphite plate of 2 mm thick.

(iv) Current Probe and Target

The port next to that for the ion source is one for a current probe, and the neighbouring port is for a target which is used for the production of radioisotopes. Each port is provided with a gate valve. The current probe is motor-driven and its tip moves between 30 cm and 150 cm from the centre of main magnet. The target is hand-operated. The bombardment by internal beams or deflected beams is selected by positioning of the target rod.

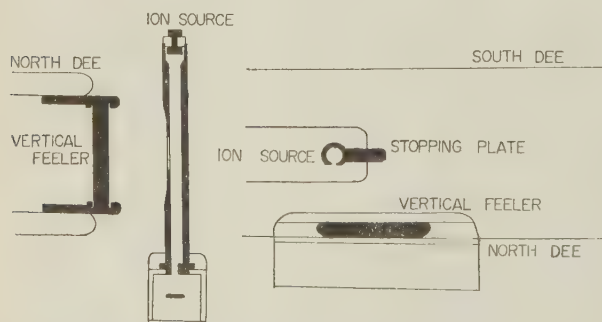


Fig. 7. Vertical feeler and ion source.

Vertical feeler and stopping plate trap the ions which start the ion source at the phases far from the peak of r -f voltage. Thus the ions which pass through the channel between both plates start the ion source at the phases near resonance.

5. Oscillator System for Ordinary Cyclotron

i) *Dees, Dee Stems and Shorting Plate*

One of the distinctive features of the oscillator system of our cyclotron is its resonant cavity of a shielded Lecher-wire type. Two dees and their stems are enclosed in a cavity with copper liners covering both the vacuum tank and the stem tank and the stems are terminated by a shorting plate. Oscillations of a push-pull mode of $\lambda/4$ in which the two dee voltages are 180° out of phase are excited in this cavity. Main advantages of adopting

Lecher-wire type cavity instead of a more usual coaxial type one which has two separated dee systems are as follows. (a) Variation of the resonant frequency in wide range is feasible, since the shorting plate is not necessary to contact with the stem tank liner and its position is easily shifted along the dee stems. (b) It is easy to insulate the dee system from the outer conductors and to suppress the so-called multipactoring effects by applying D. C. bias voltage to it. (c) It is not necessary to balance the two resonant frequencies of the two dee systems, and moreover, the resonant frequencies of parallel mode in which the two dee voltages are in phase, are enough apart from that of the required push-pull mode. These facts make adjustments of the oscillator system simpler in various respects.

Fig. 8 shows the oscillator system extracted from the vacuum tank. The whole assembly is mounted on a carriage which moves on the rails with guide bars. This has increased accessibility to the vacuum tank and has assured the reproducibility of the position of the dee system relative to the magnet centre.

Each dee consists of copper plate 4 mm thick covering the framework of silumin (an aluminium alloy). Graphite sheets 2 mm thick cover the insides of the dees and reduce the long life activities. The inside height of dee available to the beam is 7 cm. Ions are extracted from the south dee which holds a septum made of 2 mm thick curved graphite plates. The exit radius is 72 cm; the deflector channel is located on the 60° arc beginning from the centre line of the dee interface. The dee frame is bolted to the stem, so that each dee is separable from its stem.

The material of the main part of each dee stem was made by extruding a 270 mm o.d.

and 25 mm thick steel pipe together with a copper pipe covering it. Thus, the mechanically strong and round dee stems of constant diameter along their length were obtained and contacts of the shorting plate with the dee stems can be always kept in satisfactory condition wherever is the position of the shorting plate along the stems.

Two supports of each dee fixed on the carriage outside of the vacuum are equipped with mechanisms which actuate up-down and right-left positioning of each dee. The stems are electrically insulated from both the stem supports and the stem tank. Vacuum seals between the stems and the stem tank end

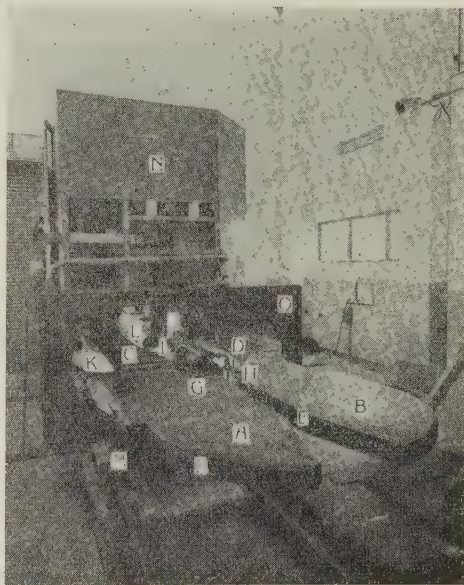


Fig. 8. Oscillator system for ordinary cyclotron
A: South dee, B: North dee, C, D: Dee stems, E: Feeler, F: Septum, G, H: Dee voltage pick-up, I: Plate coupling loop, J: Plate coupling adjuster, K: Cu strips, L: Shorting plate, M: Carriage, N: Oscillator housing, O: Flange.

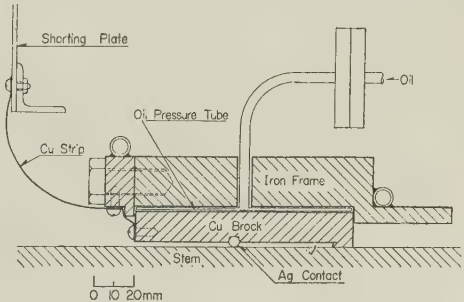


Fig. 9. Contact mechanism between shorting plate and stem.

plate are achieved with stainless steel bellows.

The shorting plate can be moved remotely from the console by means of motor drive and thus the resonant frequency can be changed from 8.4 to 12.0 Mc/sec. The contact mechanism between the shorting plate and the stems was carefully designed, since it should carry the of current up to about 4000 A peak at the maximum rating. Thirty-two copper brocks each of which has a contact line of soft-soldered 5 mm silver wire are set up around the circumference of each stem and are pressed into contact with the stem from outside by a phosphor bronze tube which is actuated by oil pressure. The copper brocks are connected with the shorting plate by flexible copper strips. Details of this part are shown in Fig. 9. With 3 mm gap and 50 cm depth of the interface between the shorting plate and the stem tank liner, the r-f voltages on the end points of the stems behind the shorting plate could be reduced to less than 0.15% of the dee voltage by putting the capacitors of about $0.02 \mu\text{F}$ at the ends of the stems.

(ii) Oscillator

The oscillator is of a grounded-grid self-excited type, two 9T71 triodes being used in parallel. Fig. 10 is a photograph of the main part of the oscillator and the circuit diagram is schematically shown in Fig. 11. The oscillator housing is placed directly on the stem tank and the connections between the oscillator tube and the plate and the cathode-loop were made as short as possible, so that the resonant frequencies of both the plate and the cathode circuits could always be kept higher than the oscillation frequency. Owing to this consideration, the adjustments of the coupling condition, required for satisfactory oscillations in wide frequency range, become very simple. The plate loop is inserted just in the middle of the two dee stems.

A coupling adjustor, an aluminium plate, which can be moved up and down by motor drive with the tank evacuated, changes the magnetic flux through the loop. The cathode loop which is just above the south dee stem had also initially a similar coupling adjustor, which was later removed since it was found unnecessary to change the cateode coupling finely.

The adjustments of the coupling conditions

required for the satisfactory oscillators efficiency are achieved mainly by changing the two capacitors, C_p and C_f , which are put in

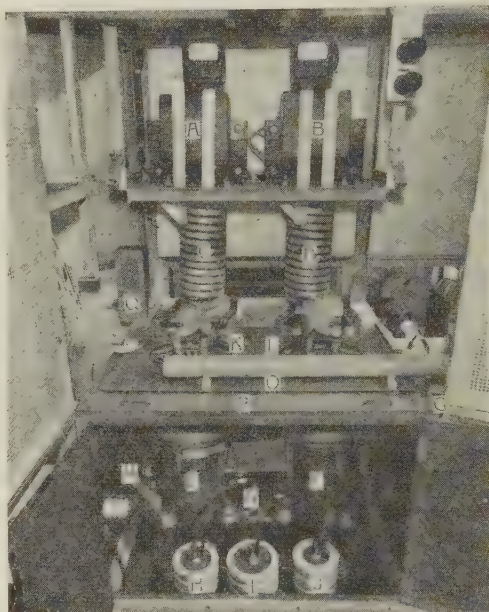


Fig. 10. Oscillator for ordinary cyclotron.

- A, B- Filament transformers (T_f),
- C, D: Choke coils (L_f),
- E, F: Oscillator tube water jacket,
- G: Ceramic condenser (C_f),
- H, I, J: Ceramic condenser (C_p),
- K, L: Grid grounding condenser (C_g),
- M, N: Water cooling pipes,
- O: A part of cathode line, P: Grounded plate,
- Q: Pick-up for grid overvoltage relay.

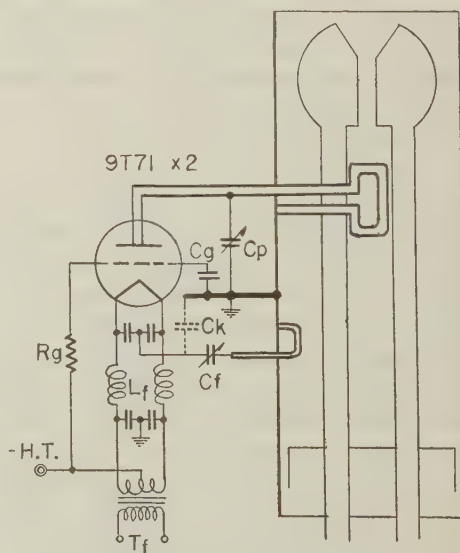


Fig. 11. Schematic diagram of osillator circiut for ordinary cyclotron.

parallel with the plates of the oscillator tubes and in series with the cathode line, respectively. These adjustments make the ratios of the plate and the cathode swing to the dee voltage to have suitable values. According to the experiences in the initial operations, it is necessary to change these coupling only stepwise and for the ranges of 1 to 1.5 Mc/sec of frequency change, nothing is needed to change except the position of the shorting plate. This is partly due to the surplus power of the oscillator and to the circumstances that in almost all cases the severe conditions are not required for the sufficient output power.

The D. C. power for the oscillator up to 250 W is supplied by means of a 6-pole mercury arc rectifier and its output D. C. voltage is kept constant within 2% by automatic control at any value continuously from 2 to 15 kV. A filter reduces ripples of the output voltages to less than 0.5%.

In the initial oscillator test without ion load, the dee-to-ground voltages up to 130 kV peak at 10 Mc/sec were attained without any significant trouble such as parasitic oscillations, except that some parts in the cavity were damaged because of their insufficient coolings. They were immediately repaired, and it was found that in the full frequency range of 8.4 to 12.0 Mc/sec satisfactory oscillations can be easily obtained.

6. Oscillator for Synchro-Cyclotron

(i) *Dee, Earth Plate and Stem*

The coaxial part of the cavity is connected to a single dee on one end and to a rotating condenser on the other end. They form a half wave length resonance circuit. The whole assembly is mounted on a carriage and has the same advantages as mentioned in § 5.

The dee consists of 4 mm copper plates covering the framework of silumin. The inside height of the most part of the dee is 3 cm., but it is 12 cm at large radius, so as to house an internal electrostatic deflector. We intended to try to extract the beam with an electrostatic deflector at $n = 1$, from the very start of the design. Therefore the radius of the dee is larger than the radius of the magnet pole for this purpose.

A steel pipe 320 mm in diameter covered by copper plate forms the stem of the dee. Two

sets of cylinders of steatite porcelain mounted inside the vacuum tank (the stem tank) support the stem at two positions.

Flexible copper plates connect the end of the stem with the stator of the rotating condenser. The dee system is insulated from the outer conductors, so that negative D. C. bias voltage can be applied to it.

The dummy dee and the earth plates are supported by the frame work which is fixed to the frange of the stem tank. They are connected electrically with the copper plates which cover the inner surface of the stem tank.

(ii) *Rotating Condenser*

It is necessary to modulate the frequency by 20% in order to accelerate protons up to the radius $n = 1$, where their energy becomes 60 MeV. Larger dee voltages together with increasing rates of frequency modulation are desirable to increase the beam intensity. These requirements increase the load on the modulator of the oscillator frequency. A variable condenser of rotating disc with many teeth around it, seems to be the best solution at present.

A induction motor to drive the rotating condenser is mounted in vacuum, like the case of the Philips synchro-cyclotron at Amsterdam⁶⁾. Fig. 12 shows the rotating condenser with its framework.

Rotation of 3000 r. p. m. is easily obtainable in vacuum, which corresponds to the modulation frequency of 1500 c/sec, and we found no trouble up to 4500 r. p. m. in the case of the mechanical test in the factory.

We have been concerned about the life of the ball bearings, which rotate at high speed in vacuum. Diffusion pump oil is used for lubrication in vacuum, and we can supply the oil from outside of the vacuum. Charging of a small amount of oil at an interval of several days has been sufficient. Several ten c. c. of oil is kept in the grooves near the bearings. Owing to a good dynamic balance, the amplitude of the vibration of the framework was reduced to about 1 micron at 3000 r. p. m.

The weight of the rotor is about 150 kg and that of the framework about 1000 kg.

During the initial operation of about 500 hours, the amplitude of vibration remained steady, and no trouble was found on the ball bearings at the overhaul.

The next thing we concerned about is the heating up of the rotor by the ohmic loss of the high frequency current. Since all the rotating parts are in vacuum, they cannot be cooled directly by water. Therefore, thermal radiation was increased by forming a black surface layer of AgS on thin silver plating. Under this silver plating thick copper plating was made on the steel body in order to carry the high frequency current. The centre shaft, which carries the rotor but does not rotate itself, is cooled by circulating oil.

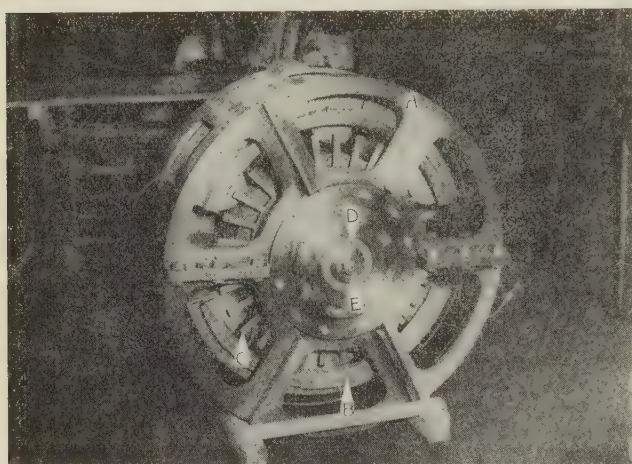


Fig. 12. Photograph of the rotating condenser.

A: Frame work, B: Stator.

C: Teeth of the rotor,

D: M: Micalex supporte, E: Centre shaft.

Many disc shaped by-pass condensers draw the high frequency current from the rotating condenser. Nevertheless the high frequency voltage of the rotor amounts to several hundred volts. Therefore we must insulate the centre shaft from the framework with two rigid insulators. The material of the insulators is Micalex, a compound of mica and glass which has good mechanical properties. A silver contact brush is mounted to protect the ball bearings from the high frequency current, which results from the stray capacity between the centre shaft and its surroundings. The condenser gap between the rotor and the stator can be adjusted by shimming plates. The gap is 1.0 ± 0.1 mm at present. The stator is supported rigidly on the framework by six Steatite porcelain cylinders. The framework is fixed at the end of the stem tank.

A large cover with wheels is used to obtain vacuum space for rotating condenser assembly,

so that it is easy to inspect them.

(iii) Oscillator

On account of the large dee-to-ground capacity ($550 \mu\text{F}$), the impedance of the stem was necessary to be lowered to 12.8Ω .

We obtain the frequency modulation from 20.3 to 24.3 Mc/sec., varying the capacity of the rotating condenser from 130 to $830 \mu\text{F}$.

The grounded-grid self-excitation system is used for the oscillator. The oscillator tube whose plate loss is 25 kW is coupled with the dee cavity by a plate loop.

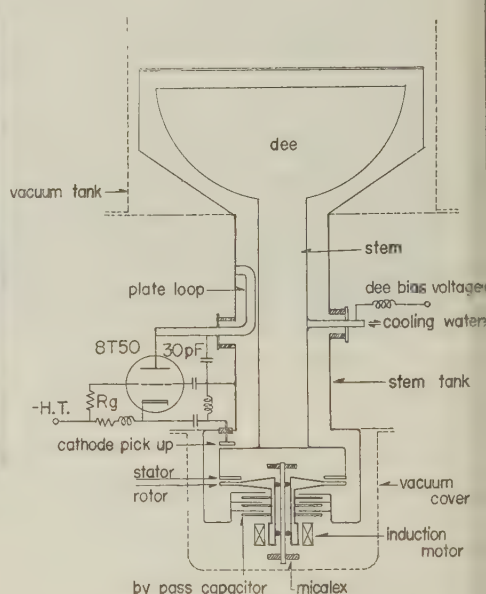


Fig. 13. Schematic diagram of the synchro-cyclotron oscillator.

The feedback voltage is picked up capacitively near the condenser end of the stem, in order to suppress the parasitic oscillation, which is caused by a higher resonance mode of the dee stem. The quality value, "Q" of the dee system was considerably lower than the expected value. Even after some improvements, it has remained at 900-1200 which is about 1/2 of the expected value. Consequently, the oscillation was somewhat difficult on the lower frequency side. We put $30 \mu\text{F}$ capacity in parallel to the plate of the tube. Then, the amplitude of the plate swing increased. The amplitude of the cathode swing in the lower frequency has increased by inserting an inductance in parallel to the cathode capacity of the tube. The modulation of the amplitude remains 2:1 after the improve-

ment. Although the dee voltage can be raised over 10 kV against the spark over of the condenser gap, temperature rise of the rotating condenser limits the dee voltage up to 7 kV for continuous operation.

§ 7. Vacuum System

The volume of vacuum space of this cyclotron is about 9,000 l, and the total surface area of materials in contact with vacuum is about $1.4 \times 10^6 \text{ cm}^2$. Most of the materials consist of copper, soft steel and stainless steel.

They have been well polished and especially soft steel was plated with nickel as possible, so that a quantity of outgassing is reduced to $1 \times 10^{-10} \text{ mmHg l/sec} \cdot \text{cm}^2$. The total leakage is less than $2 \times 10^{-4} \text{ mmHg l/sec}$.

Most of the structures were welded together by the Heliarc process and a few parts were soldered with silver, and soft soldering was entirely avoided. Vacuum seals are of double grooves fitted with either "O" ring or square gasket, designed to be metal-to-metal contact at the flanges.

A scheme of the pumping system is shown in Fig. 14. The main pump is 32 inch oil diffusion pump, backed by a 10 inch ordinary oil diffusion pump in order to be able to purify the oil in the main pump. So that, a sufficiently good end vacuum was obtained without

any cooling baffle or trap.

The heater wattage of the main pump is 5.2 kW, and the speed of evacuation at $5 \times 10^{-5} \text{ mmHg}$ is 20,000 l/sec for air, 35,000 l/sec for helium and 37,000 l/sec for hydrogen gas respectively. A pressure of $1 \times 10^{-6} \text{ mmHg}$ is obtained as the end vacuum measured with a high speed ionisation gauge without liquid nitrogen trap. In initial rough evacuation, three rotary pumps of 3,000 l/min in speed are used.

When the cyclotron is in operation, the pressure is about $5 \times 10^{-6} \text{ mmHg}$, and this value is obtained within ninety minutes after switching on heaters of oil diffusion pumps.

In the synchro-cyclotron case, the tank which houses the rotating condenser is evacuated differentially with a 6 inch oil diffusion pump.

Most of the vacuum valves are operated by compressed air.

§ 8. Cooling System

As cooling materials, transformer oil is used for the coils of the main magnet and for the deflector, well-water for the vacuum pumps and pure water for all the other parts to be cooled. Pure water is obtained by the method of ion exchange. With a few exceptions, the flow of these cooling materials are controlled so that the rise of temperature is less than 10°C . Warmed pure water and oil are cooled in a heat exchanger by water circulating from a pool of 25 meters square and 2 meters deep.

As the materials of the pipes for pure water, iron was perfectly avoided. Hard vinyl tubes were used for the main pipes and copper or soft vinyl tubes were also used locally. But afterwards it has become clear that soft vinyl tubes are very weak for rise of temperature, so they have been replaced, after one year use, by synthetic rubber tubes for aeroplanes.

A valve is installed at every branch of the cooling system to control flow adequately. A thermometer of thermister type is installed at the outlet of any cooling pipe where it is especially required to measure the temperature remotely in operating condition. This served very much to prevent any accidents.

§ 9. Control System

The control system contains, as is usually

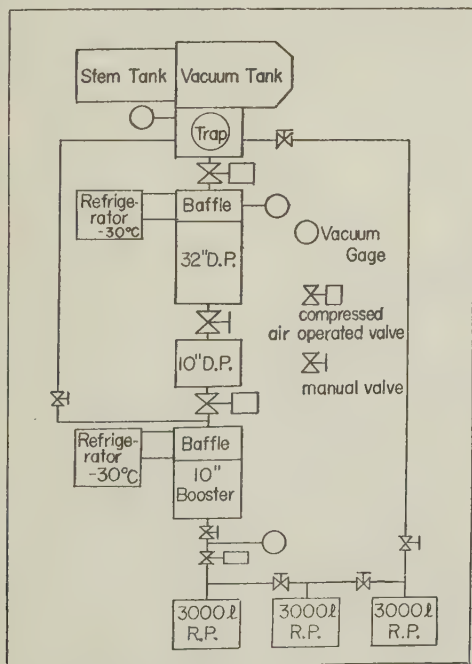


Fig. 14. Diagram of the vacuum system.

so, "on" and "off" of every element, regulation of voltages and currents, position control of mechanical elements by motor drive, interlocks for safety, alarms and indications of accidents and various other indications.

The control console consists of thirty seven unit panels of drawer type which are exchangeable one another, and each unit provides some meters, switches, handles for regulation and lamps of three colours for indication.

All the control lines which interlock more than two components of the machine mutually are brought together in a cross-connect panel to be easily reorganized. Relays, except the peculiar ones to each component, are also assembled together on a relay panel for easy keeping.

At the time of any accident, the defective component itself and the related ones are automatically switched off, the alarm is rung, and an indicator in the central indicator panel indicates the defective part of the components.

Mechanical movements of the ion source, deflector, dees, capacity compensators, current probe, shorting plate and slits are driven by motors remotely from the control console. And their positions are indicated at the console by means of celsin motors or voltages of helical potentiometers attached coaxially to the rotation axes. These remote control mechanisms are indispensable to find out rapidly an optimum condition of the cyclotron in operation.

To prevent any fatal damage of the machines or any danger to human lives as fast as possible, ten emergency switches in total are arranged in every room shown in Fig. 1. Any one of these emergency switches stops the electric sources of all the components except the cooling and the vacuum system.

§ 10. Beam Focusing System for Ordinary Cyclotron

The leading ideas of the design of the focusing system are such that, first, we can obtain nearly the best condition of the beam without changing the position of the experimental apparatus whenever the kind or the energy of the beam is changed, and that, secondly, we may lead the beam in several different directions in the measuring room and can make arrangements of several experiments independently. Fig. 15 shows the out-line of the beam focusing system. The beam which leaves the r-f deflector goes through a magnetic shielding channel, a pair of quadrupole magnets and a sector magnet. Then it is lead to the measuring room through the concrete shielding wall and is focused to any one of the three different positions which are apart from the cyclotron by more than 8 meters. The first course supplies the beam to the large scattering chamber and the second straight course supplies the beam to the experiments of neutron or gamma-ray. The third course, into which the sector magnet

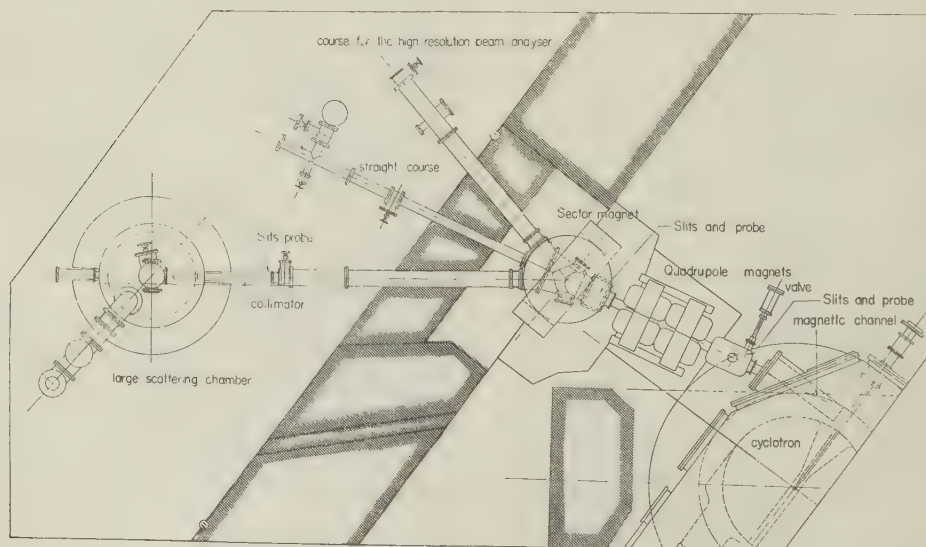


Fig. 15. Beam focussing system.

deflects the beam to the opposite direction against the first course by changing the polarity of its field, supplies the beam to the analyser system of high energy resolution. This system is now under construction.

The magnetic shielding channel is shown in Fig. 16 and its position is indicated in Fig. 15. This device is needed lest the beam should pass too close to the yoke of main magnet.

The coil currents of the pair of quadrupole magnets are supplied separately by stabilized current sources, and controlled independently. The entrance edge of the sector magnet can be turned around and the entrance angle of the beam to the field boundary can be changed from -30 degrees to $+30$ degrees.

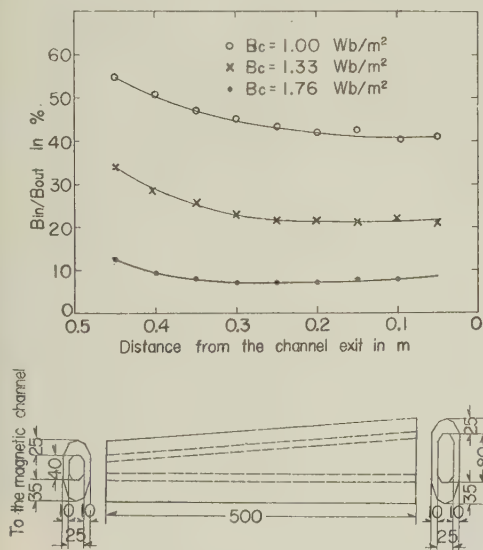


Fig. 16. magnetic shielding channel and the rate of field reduction.

The characters of the quadrupole lens, of the sector magnet and of the combined lens are calculated and then are verified by the stretch wire method and also with a Polonium- α source and a CsI scintillator. By changing the coil currents of the three magnets, we can obtain the first order focusing in horizontal and vertical directions even when the positions of the source and the image are varied considerably and the kind and the energy of the beam are changed. In this system, we obtained the momentum resolution of 0.2% with a Po- α source.

The positions of current probes and slits are shown in Fig. 15. Some of them are in-

sulated and the currents into them can be read at the console. These currents can guide the cyclotron operation and the adjustments of the three coil currents of the focusing system. And, we can pass the considerable parts of the external beam through a slit of 6 mm in width and placed before the experimental equipments, the best image being 5 mm wide and 10 mm high. The data of the coil currents for the actual beam are analysed by the optical formula⁶⁾. These analysis gave the following conclusions about the nature of the cyclotron external beam.

(1) The beam has a rather sharp source point in the horizontal direction but its position changes considerably according to the conditions of the cyclotron operation. (2) The source point in the vertical direction is not so sharp but the divergence in this direction is very small. (3) The spreads of beam energy are rather small and the energy resolution at half maximum may be about 0.5%. The details of the design, analysis, construction, and performances of this system have been described elsewhere⁶⁾.

§ 11. Scattering Chamber for Ordinary Cyclotron

The scattering chamber is 100 cm in inner diameter and 40 cm in height and has thirty three ports on its side wall to which many detectors can be attached simultaneously. By this method, we can obtain a high efficiency of measurements and it is suitable for the common usage by a large number of researchers. The ports are distributed at intervals of five degrees and cover the scattering angles between 10° and 170° . Further, a turntable of 84 cm in diameter is provided in vacuum within the chamber and detectors attached to it can be set any desired angle. Graduation marks are scratched with interval of $1/10^\circ$ on the periphery. The accuracy of the graduation is within $20''$. The axis of this turntable is supported by precision ball bearings and is coaxial with the target supporting rod. Both can be turned separately. Fig. 17 shows the scattering chamber and its accessories. We referred in many respects to the 60-inch scattering chamber by Yntema and White⁷⁾.

The beam collimator in front of the scattering chamber contains two defining slits 80 cm apart and four antiscattering slits. Each

slit is fixed at the end of a cylinder and these cylinders are inserted into a guide cylinder. Thus the change of slit dimensions is easily accomplished.

The beam collector is a Farady cup of 7.6 cm in inner diameter and 22 cm in length. Two small electromagnets and a guard ring is provided to suppress the effects of secondary electrons.

For the precise and easy alignment of the scattering chamber to the incident beam, the functions of the adjustment mechanisms are as follows. The target holder can be moved in two directions perpendicular to each other in horizontal plane and the target surface is

placed at the position of the rotation axis of the turntable. The beam collimator has adjustment screws for up and down, and for rotations in a vertical and a horizontal plane. The support of the detector slit on the turntable has also adjustment screws for up and down and for rotation in a horizontal plane. The support of the scattering chamber itself consists of three columns of steel frame. Each has screws or wheels for leveling and for translation in the horizontal plane or rotation in a horizontal plane around the axis through the front defining slit of the beam collimator.

The scattering chamber is evacuated with a 6-inch oil diffusion pump and a 500 l/min rotary pump. A liquid nitrogen trap is provided at the lid of the scattering chamber, and a vacuum evaporator can be attached also to the lid. The exchange of targets is possible without breaking the vacuum. Fig. 18 shows the combination of the focusing magnets, beam ducts and the scattering chamber.

We have constructed also a multiplate camera which is modified from the one by Allred et al.⁸⁾. Nuclear plates are placed at intervals of 2.5 degrees between 7.5 and 172.5 degrees of scattering angles. Both a ring of single slit for foil targets and a ring of double slits for gas targets are provided. They are interchanged each other in the respective use. The multiplate camera is put entirely in the scattering chamber and fitted to a conical fit on the turntable.

§ 12. Shielding

An outline of the shielding has been shown already in Fig. 1. The side walls and the ceiling are made of ordinary concrete of 150 cm and 96 cm thick respectively. The water tank which consists the movable part of the shielding walls is 150 cm thick. The space around the beam ducts where the wall is penetrated is filled up with blocks of heavy concrete, of iron and of paraffin. And other openings in the shielding walls are filled with ordinary concrete blocks or small water tanks.

Some examples of the results of surveying the neutron flux outside of the shielding, which are obtained with a Nuclear-Chicago model 2112 ratemeter and model DN3 neutron probe, are as follows. When deuterons are

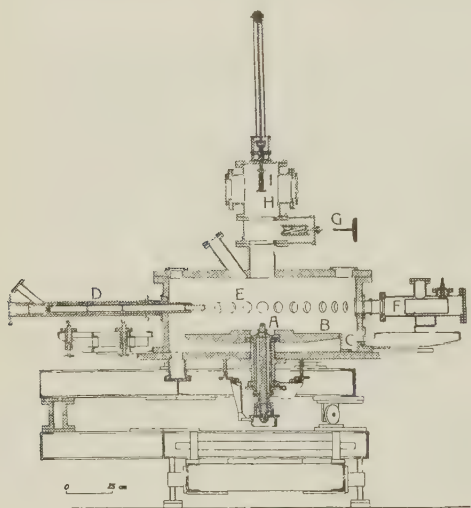


Fig. 17. 100cm scattering chamber.

- | | |
|---------------------------|----------------------|
| A: Target holder | F: Faraday cup |
| B: Turntable | G: Gate valve |
| C: Vernier of graduations | H: Vacuum evaporator |
| D: Collimator | I: Target changer |
| E: Holes on the side wall | |



Fig. 18. Photograph of the beam focussing system and the scattering chamber.

accelerated to 19 MeV and its intensity is $0.05 \mu\text{A}$ at the scattering chamber, neutron fluxes are (1) $30 \text{ n/cm}^2/\text{sec}$ at the immediate vicinity of the main shielding wall and (2) $0.3 \text{ n/cm}^2/\text{sec}$ at the control room. When protons of 57 MeV and $1 \mu\text{A}$ are accelerated in the synchro-cyclotron, the neutron fluxes at the places above described are (1) $10 \text{ n/cm}^2/\text{sec}$ and (2) less than $0.1 \text{ n/cm}^2/\text{sec}$ respectively.

§ 13. Operation of Ordinary Cyclotron

After general assembling had been finished we accelerated protons at the frequency of 9.7 Mc/sec for the first time on September 28, 1957. As soon as the magnetic field was adjusted to the resonance value, we obtained a beam of $300 \mu\text{A}$ at the exit radius. In the next day a deflected beam of $30 \mu\text{A}$ was obtained after some adjustments of deflector position. We assured successively that stable internal and deflected beams were obtained in the expected range of energy. After setting the focusing magnets, beam ducts and scattering chamber, we began experiments of nuclear reactions from January, 1958.

A few kinds of trouble have been experienced in the operation of long time duration such as the cracking of the insulators of Steatite- or ordinary porcelain. Such difficulties have been overcome by the protection against the discharge or by the increase of the air cooling.

The performances are listed in Table I (§1). The maximum current obtained at the focus point of the straight section through a slit of $1 \text{ cm} \times 1 \text{ cm}$ is $4 \mu\text{A}$ of protons of 14 MeV. During the ten months since January, 1958, various experiments on (1) $p-p$, $p-d$, $p-\alpha$, $\text{He}^3-\alpha$ and $\alpha-\alpha$ scatterings, (2) (p, p) , (p, p') , (d, n) , (p, n) and (α, p) reactions, (5) production of several radioisotopes have been performed. The cyclotron is working in full of 24 hours except Sundays and the days of periodical inspection which are arranged once in ten days. The working efficiency is about 55% for 24 hours of a working day.

§ 14. Initial Operation of Synchro-Cyclotron

During the period of use of the ordinary cyclotron beam for experiments of various nuclear reactions, we took a period of about a month for the initial operation of synchro-cyclotron in May, 1958. Since we intended from the very start to try the beam extraction at $n = 1$ proposed by Hamilton and Lipkin⁴⁾, our main object was to find how much of the internal beam could be brought out until $n = 1$ by eliminating the various causes of loss of the beam between $n = 0.2$ and 1. Azimuthal inhomogeneities of the magnetic field which are negligible in our case, the ion source configuration, its position and the dee bias voltage were found to be important

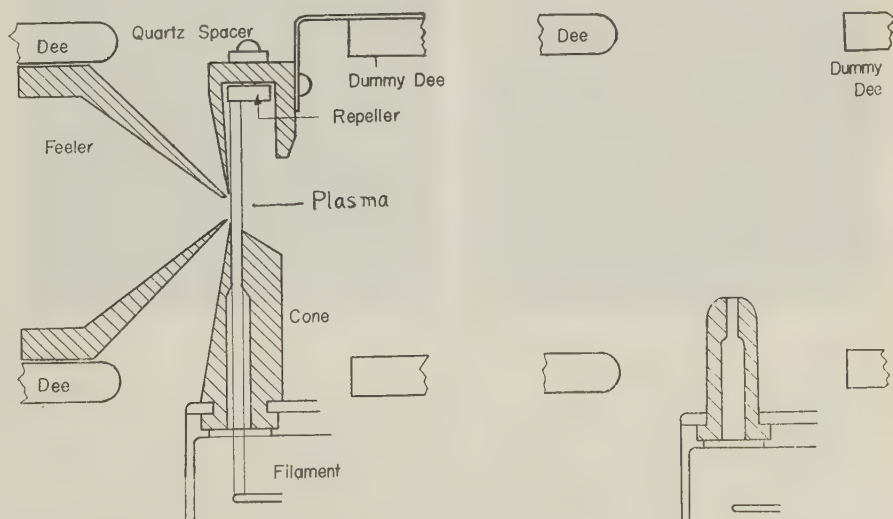


Fig. 19. Arrangement of ion source and feeler for the synchro-cyclotron.

(a) Optimum arrangement.

(b) Usually accepted arrangement.

factors for the efficiency. For example, with an usually accepted type of ion source such as shown in Fig. 19(b), only about 30% of the circulating beam inside $n=0.2$ could

arrive at $n=1$.

Among the various ion source configurations, that which is shown in Fig. 19(a) yielded the most intense beam at $n=1, 0.8 \mu\text{A}$ for the

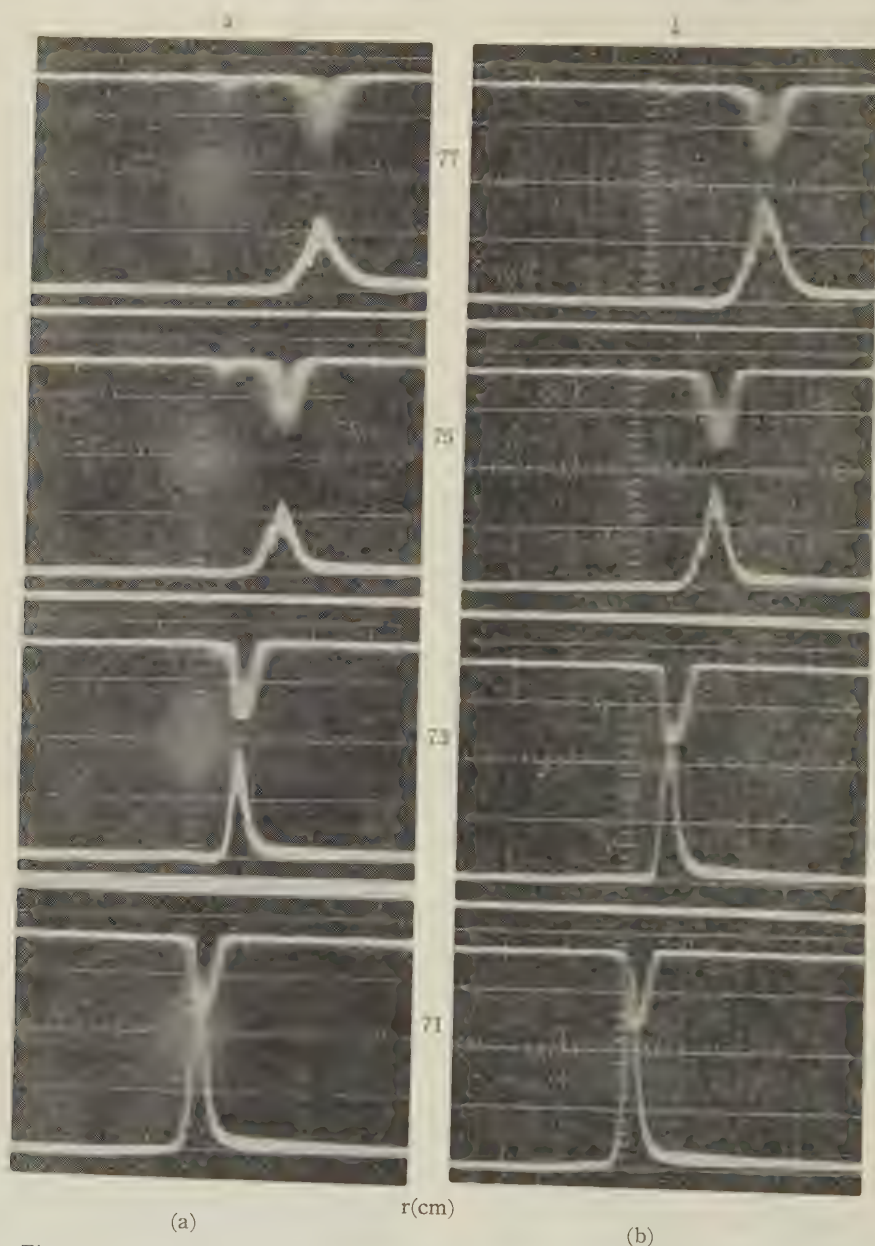


Fig. 20. Oscilloscope patterns of the internal beam pulses at $n > 0.2$ (modulation cycle = 930 c/sec).

(a) Dee bias voltage $V_B = -650\text{V}$, (b) $V_B = -120\text{V}$.

In each figure the lower pattern is due to the probe current and the upper one is due to the neutron pulses coming from a plastic scintillator situated in the cyclotron room. The neutron pulses due to the beam hitting the dee by vertical blow-up near $n=0.2$ (indicated by arrows) are more distinctive for larger dee bias voltage. It should be noted also that the reduction of the probe current is more striking in this case.

dee voltage of 7 kV, which is about 80% of the beam intensity inside $n = 0.2$, under the optimum conditions, where the ion source was slightly shifted north from the magnet centre and the magnitude of the dee bias voltage was reduced to as low as 100 volts negative. The effect of the dee bias voltage is illustrated by the oscilloscope patterns in Fig. 20.

In the second test period from December, 1958 to January, 1959, we set a 65° arc electrostatic deflector channel at a radius near $n=1$ inside the dee, and from 70 to 80% of the circulating beam up to $n=1$ could be deflected on to an area of 10 cm wide and 3 cm in height at the prescribed exit port of the vacuum tank. This beam size has been reduced to an area of 2 cm in diameter by inserting inside the tank a magnetic channel in which the magnetic field increases with radius. This beam will be brought to the experimental room through a pair of quadrupole focusing magnets in the near future. The beam intensity inside $n = 0.2$ is at present limited to about $1 \mu\text{A}$ for continuous operation because the dee voltage can not exceed about 7 kV as is mentioned in § 6. Details on the beam extraction at $n=1$ will be reported elsewhere.

Acknowledgements

The authors wish to express their cordial thanks to the members of the Technical Committee for the Cyclotron (Semmon-Iinkai), under whose advices the fundamental design of this cyclotron has been performed. Thanks are also due to Tokyo-Shibaura Electric Co., Ltd. for the detailed design and careful construction.

The author would also like to acknowledge the technical assistances of Messrs. H. Adachi, T. Yamada, Y. Miyazawa, and K. Omata of this Institute.

References

- 1) H. Kumagai et al.: J. Phys. Soc. Japan **14** (1959) 1.
- 2) H. Kumagai et al.: INSJ-2, June 13, 1957.
- 3) R. S. Livingston and R. J. Jones: Rev. Sci. Instrum. **25** (1954) 552.
- 4) D. R. Hamilton and H. J. Lipkin: Rev. Sci. Instrum. **22** (1951) 783.
- 5) F. A. Heyn and J. J. Burgejon: Philips Tech. Rev. **14**, (1953) 263.
- 6) K. Matsuda et al.: INSJ-14, January 15, 1959.
- 7) J. L. Yntema and M. G. White: Phys. Rev. **95** (1954) 1226.
- 8) J. C. Allred et al.: Rev. Sci. Instrum. **22** (1951) 191.

On the Variation Principle in the Kinetic Theory of Dense Gases, I.

By Terutosi MURAKAMI

*Department of Applied Science, Faculty of Engineering
Kyushu University, Fukuoka, Japan*

(Received September 2, 1959)

The variation principle in the kinetic theory of gases is extended to the case of a dense gas made of rigid-sphere molecules with the finite radius. The solution of Enskog's first approximation equation for the dense gas of rigid-sphere molecules is derived from the variation principle. The local entropy production per unit time is the maximum in this variational principle. The correction to the entropy due to imperfectness of the gas is calculated from the virial expansion of the equation of state for a rigid-sphere gas.

§ 1. Introduction

The variation principle in the kinetic theory of gases was established by Hellund and Uehling¹⁾, Curtiss and Hirschfelder²⁾, and Ono³⁾. Especially, Ono showed that this principle has a close relation to the extremum of the production of entropy in the thermodynamics of irreversible processes. Up to now, however, this variation principle has been proved only for a dilute gas.

The purpose of the present paper is to generalize this principle to the case of a slightly dense gas consisting of rigid-sphere molecules, based on Enskog's modification of the Boltzmann equation⁴⁾⁵⁾⁶⁾, as a first step to furnish the method of solving the problems in the kinetic theory of fluids from the thermodynamical point of view.

In Enskog's theory⁴⁾ of a dense gas the molecules are no longer points but spheres of finite radius, and there appears the collisional transfer due to the finite size of molecules in addition to the ordinary fluxes arising from the flow of molecules across the surface. From these flux vectors we can obtain the thermodynamic expression for the local production of entropy by means of the Gibbs relation.

The entropy of a dilute gas can be defined in terms of the singlet molecular distribution function, and is equal to the minus of Boltzmann's H -function in the case of the ideal gas. Then the local entropy production per unit time can be derived from the entropy balance, and given by the collisional term in the Boltzmann equation. In the present case, however, the correction to the entropy due to

imperfectness of the gas should be taken into account. If one regards this correction as a small quantity, this can be achieved by adding the equilibrium value of the additional entropy calculated from the virial expansion of the equation of state. After all, the entropy production per unit time at each point of space is calculated by means of the modified Boltzmann equation.

Thus, in the same manner as in the case of the dilute gas⁴⁾, it will be shown that Enskog's first approximation solution is the solution which maximizes the entropy production to the first order under the condition that the entropy production in terms of molecular expressions is equal to the one based on the Gibbs relation in the thermodynamics of irreversible processes.

§ 2. The Modified Boltzmann Equation for a Dense Gas

Let us consider briefly Enskog's modification of the Boltzmann equation for a dense gas consisting of rigid-sphere molecules, in which the molecular encounters are instantaneous and consequently binary irrespective of its density.

We shall define the singlet distribution function $f(\mathbf{r}, \mathbf{v}, t)$ in such a way that the probable number of molecules with positional coordinates in the range $d\mathbf{r}$ about $\mathbf{r}$ and with velocities in the range $d\mathbf{v}$ about $\mathbf{v}$ is $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{r}d\mathbf{v}$, f being normalized to the number density n :

$$\int f(\mathbf{r}, \mathbf{v}, t)d\mathbf{v} = n(\mathbf{r}, t). \quad (2.1)$$

The variation of this function with time obeys the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{\mathbf{F}}{m} \cdot \nabla_v f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}, \quad (2.2)$$

where $\mathbf{F}$ is the external force acting upon a molecule, m the mass of a molecule, and $(\partial f / \partial t)_{\text{coll}}$ the collisional change of distribution function. The collision term of Enskog's modification⁽⁴⁾⁽⁵⁾ is given in the form

$$\begin{aligned} \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = & \iint \left\{ \chi \left(\mathbf{r} + \frac{\sigma}{2} \mathbf{k} \right) f'(\mathbf{r}, \mathbf{v}', t) f_1(\mathbf{r} + \sigma \mathbf{k}, \mathbf{v}_1, t) \right. \\ & \left. - \chi \left(\mathbf{r} - \frac{\sigma}{2} \mathbf{k} \right) f(\mathbf{r}, \mathbf{v}, t) f_1(\mathbf{r} - \sigma \mathbf{k}, \mathbf{v}_1, t) \right\} \\ & \times \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \end{aligned} \quad (2.3)$$

where $\mathbf{k}$ is the unit vector in the direction of line of centers of molecules, σ the diameter of a molecule, $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}$ the relative velocity, and $\mathbf{v}, \mathbf{v}_1$ the velocities of the molecules after the collision characterized by $\mathbf{v}, \mathbf{v}_1$ and $\mathbf{k}$. Here we used the notation χ for Enskog's probability factor⁽⁴⁾⁽⁵⁾ by which the frequency of collisions in a gas made up of rigid-sphere molecules differs from that in a gas made up of point molecules. The value of χ in an equilibrium uniform gas depend only on the density. But in a non-uniform gas the value of χ may be expected to depend on the spatial derivatives of the density.

If the conditions in gas are slowly varying in space, we may use the local equilibrium value χ^0 for χ to the second approximation, and expand $f(\mathbf{r} + \sigma \mathbf{k}, \mathbf{v}, t)$ and $\chi^0(\mathbf{r} + \sigma \mathbf{k}, t)$ in a power series in σ , and retain the terms only up to the second. Then (2.3) may be written in the form:

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \sum_{i=1}^6 J_i(f, f_1), \quad (2.4)$$

where

$$J_1 \equiv \chi^0 \iint (f' f'_1 - f f_1) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-1)$$

$$J_2 \equiv \sigma \chi^0 \iint \{ \mathbf{k} \cdot (f' \nabla f'_1 + f \nabla f_1) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-2)$$

$$J_3 \equiv \frac{\sigma}{2} \iint (\mathbf{k} \cdot \nabla \chi^0) (f' f'_1 + f f_1) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-3)$$

$$J_4 \equiv \frac{\sigma^2}{2} \chi^0 \iint \{ \mathbf{k} \mathbf{k} : (f' \nabla \nabla f'_1 - f \nabla \nabla f_1) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-4)$$

$$J_5 \equiv \frac{\sigma^2}{2} \iint (\mathbf{k} \cdot \nabla \chi^0) \{ \mathbf{k} \cdot (f' \nabla f'_1 - f \nabla f_1) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-5)$$

$$J_6 \equiv \frac{\sigma^2}{8} \iint (\mathbf{k} \mathbf{k} : \nabla \nabla \chi^0) (f' f'_1 - f f_1) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v}_1, \quad (2.4-6)$$

where f'_1 and f_1 are, respectively, $f_1(\mathbf{r}, \mathbf{v}_1, t)$ and $f_1(\mathbf{r}, \mathbf{v}_1, t)$.

From (2.2) and (2.4) we obtain our fundamental equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{\mathbf{F}}{m} \cdot \nabla_v f = \sum_{i=1}^6 J_i(f, f_1), \quad (2.5)$$

§ 3. Equation of Change and Flux Vectors

Let us consider the fluxes of various molecular properties, such as mass, momentum and kinetic energy, across a surface element in a dense gas. Let us denote one of these properties by ψ , and the average $\bar{\psi}$ of this property at each point of space is given by

$$n \bar{\psi} = \int \psi f d\mathbf{v}. \quad (3.1)$$

Then the stream velocity $\mathbf{v}_0$ is defined by

$$\rho \mathbf{v}_0 = \int m \mathbf{v} f d\mathbf{v}, \quad (3.2)$$

in which $\rho = nm$ is the mass density.

Multiplying (2.5) by ψ and integrating over the velocity space, we find

$$\begin{aligned} \frac{\partial (n \bar{\psi})}{\partial t} + \nabla \cdot n \bar{\psi} \mathbf{v} - n \left\{ \frac{\partial \bar{\psi}}{\partial t} + \mathbf{v} \cdot \nabla \bar{\psi} + \frac{\mathbf{F}}{m} \cdot \nabla_v \bar{\psi} \right\} \\ = \sum_{i=1}^6 I_i(\psi), \end{aligned} \quad (3.3)$$

where

$$I_i(\psi) = \int \psi J_i d\mathbf{v}. \quad (3.4)$$

If ψ is one of the summational invariants the right hand side of (3.3) is, after a rather cumbersome calculation shown in Appendix I, reduced to the following form:

$$\sum_{i=1}^6 I_i(\psi) = -\nabla \cdot \mathbf{J}_c(\psi) + \mathcal{O}(\psi), \quad (3.5)$$

where

$$\begin{aligned} \mathbf{J}_c(\psi) \equiv & \frac{\sigma^3}{2} \chi^0 \iiint (\psi' - \psi) f f_1 \mathbf{k} (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v} d\mathbf{v}_1 \\ & + \frac{\sigma^4}{4} \chi^0 \iiint (\psi' - \psi) f f_1 \left(\mathbf{k} \cdot \nabla \ln \frac{f_1}{f} \mathbf{k} \right) \\ & \times (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v} d\mathbf{v}_1, \end{aligned} \quad (3.6)$$

$$\begin{aligned} \mathcal{O}(\psi) \equiv & \frac{\sigma^3}{2} \chi^0 \iiint f f_1 \{ \mathbf{k} \cdot \nabla (\psi' - \psi) \} (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v} d\mathbf{v}_1 \\ & + \frac{\sigma^4}{4} \chi^0 \iiint f f_1 \left(\mathbf{k} \cdot \nabla \ln \frac{f_1}{f} \right) \{ \mathbf{k} \cdot \nabla (\psi' - \psi) \} \\ & \times (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{v} d\mathbf{v}_1. \end{aligned} \quad (3.7)$$

As was pointed out by Hirschfelder et al⁽⁶⁾, $\mathbf{J}_c(\psi)$ is the contribution of the collisional transfer of ψ to the flux vector. In addition to the above-mentioned collisional transfer, there exists a flux due to the flow of molecules across the surface moving with the mass average velocity $\mathbf{v}_0$, given by

$$\mathbf{J}_k(\psi) \equiv \int \psi \mathbf{V} f d\mathbf{v} . \quad (3.8)$$

where $\mathbf{V} = \mathbf{v} - \mathbf{v}_0$ is called the peculiar velocity. On the other hand, there remains the term $\Phi(\psi)$ given by (3.7). This term has not been taken into consideration by other authors for the transfer of kinetic energy, but it is necessary to obtain the correct expression for the energy balance equation. It gives a certain kind of energy source.

We shall derive the hydrodynamic equations from the general equation of change (3.3), by considering the following three kinds of the summational invariants, 1, $m\mathbf{V} = m(\mathbf{v} - \mathbf{v}_0)$ and $mV^2/2 = m(\mathbf{v} - \mathbf{v}_0)^2/2$ as ψ .

(I) *The equation of continuity*: Let us consider the case of the first summational invariant, 1. Then, using (2.1) and (3.2) we obtain the continuity equation:

$$\frac{Dn}{Dt} + n\mathbf{v}_0 \cdot \nabla = 0 , \quad (3.9)$$

where $\mathbf{J}_c$ and Φ , given respectively by (3.6) and (3.7), vanish identically, and D/Dt denotes the hydrodynamic operator $\partial/\partial t + \mathbf{v}_0 \cdot \nabla$.

(II) *The equation of motion*: Let us consider the case of the second summational invariant, $m\mathbf{V} = m(\mathbf{v} - \mathbf{v}_0)$. Then we obtain, from (3.3),

$$\rho \frac{D\mathbf{v}_0}{Dt} + \nabla \cdot \mathbf{P} = n\mathbf{F} , \quad (3.10)$$

where $\mathbf{P}$ is given by

$$\mathbf{P} = \mathbf{P}_k + \mathbf{P}_c , \quad (3.11)$$

$$\mathbf{P}_k = \int m \mathbf{V} \mathbf{V} f d\mathbf{v} , \quad (3.11-K)$$

and

$$\mathbf{P}_c = \mathbf{J}_c[m\mathbf{V}] . \quad (3.11-C)$$

We can immediately see that (3.10) is the equation of motion and $\mathbf{P}$ is the pressure tensor.

(III) *The equation of energy balance*: We have only to put $mV^2/2 = m(\mathbf{v} - \mathbf{v}_0)^2/2$. Here we should take account of the dependence of $\mathbf{v}_0$ on the spatial coordinates. Then we have

$$n \frac{D\hat{U}}{Dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v}_0 = 0 , \quad (3.13)$$

where $\hat{U}$ is the kinetic contribution to the internal energy per molecule, and $\mathbf{q}$ is the thermal energy flux, respectively, given by

$$n\hat{U} = \frac{1}{2} m \int V^2 f d\mathbf{v} , \quad (3.13)$$

and

$$\mathbf{q} = \mathbf{q}_k + \mathbf{q}_c \quad (3.14)$$

$$\mathbf{q}_k = \frac{1}{2} m \int V^2 \mathbf{V} f d\mathbf{v} \quad (3.14-K)$$

$$\mathbf{q}_c = \mathbf{J}_c[\frac{1}{2} m V^2] \quad (3.14-C)$$

Hereafter the mark $\wedge$ is used to denote the quantity per molecule. In derivation of the above equation, it should be noted that $\Phi[mV^2/2]$ does not vanish and is given by

$$\Phi[\frac{1}{2} m V^2] = -\mathbf{P}_c : \nabla \mathbf{v}_0 , \quad (3.15)$$

The local temperature T defined by

$$\frac{3}{2} nkT = \frac{1}{2} m \int V^2 f d\mathbf{v} , \quad (3.16)$$

which leads to

$$n\hat{U} = \frac{3}{2} nkT . \quad (3.17)$$

If the system is not so far from equilibrium, we may choose as the zeroth approximation to the distribution function the Maxwell function given by

$$f^0(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left\{ -\frac{m(\mathbf{v} - \mathbf{v}_0)^2}{2kT} \right\} , \quad (3.18)$$

where n , $\mathbf{v}_0$, and T are respectively given by (2.1), (3.2) and (3.16) and are generally functions of the spatial coordinates.

Then, the distribution function f may be written in terms of a perturbation function ϕ defined by

$$f = f^0(1 + \phi) . \quad (3.19)$$

From (2.1), (3.2), (3.16) and (3.19) we can prove the following relations:

$$\int f^0 \phi d\mathbf{v} = 0 , \quad (3.20-I)$$

$$\int \mathbf{v} f^0 \phi d\mathbf{v} = 0 , \quad (3.20-II)$$

$$\int \frac{1}{2} m V^2 f^0 \phi d\mathbf{v} = 0 . \quad (3.20-III)$$

If we use (3.19) and (3.20), the pressure tensors given by (3.11) are written as the first approximation in the forms

$$\mathbf{P}_k = nkT \mathbf{U} + m \int \mathbf{V} \mathbf{V} f^0 \phi d\mathbf{v} \quad (3.21-K)$$

and

$$P_e = \frac{2}{5}nb\chi^0 \left[\frac{5}{2}nkT\mathbf{U} + m \int V V f^0 \phi dv \right] - \tilde{\omega} \left[\frac{6}{5} \cdot \frac{\mathbf{S}}{T} + \frac{\mathbf{v} \cdot \mathbf{v}_0}{T} \mathbf{U} \right], \quad (3.21-C)$$

where $\mathbf{U}$ is the unit tensor, $\mathbf{S}$ the rate of shear tensor defined by

$$S_{ij} = \frac{1}{2} \left[\frac{\partial v_{0j}}{\partial x_i} + \frac{\partial v_{0i}}{\partial x_j} \right] - \frac{1}{3} \delta_{ij} (\mathbf{v} \cdot \mathbf{v}_0), \quad (3.22)$$

and

$$b = \frac{2}{3} \pi \sigma^3 \quad (3.23)$$

$$\tilde{\omega} = \frac{4}{9} n^2 \sigma^4 \chi^0 (\pi m k T^3)^{1/2}. \quad (3.24)$$

Then the total pressure tensor is

$$\mathbf{P} = \left[p^0 + \tilde{\omega} \left(-\frac{\mathbf{v} \cdot \mathbf{v}_0}{T} \right) \right] \mathbf{U} + \left(1 + \frac{2}{5} nb\chi^0 \right) m \int V V f^0 \phi dv - \frac{6}{5} \tilde{\omega} \frac{\mathbf{S}}{T}, \quad (3.25)$$

where

$$p^0 = nkT(1 + nb\chi^0), \quad (3.26)$$

which is the equilibrium hydrostatic pressure at the local temperature and density, differing from that of the ideal gas case by $n^2 k T b \chi^0$. This means that the gas is not ideal but imperfect. On the other hand the equation of state in equilibrium for rigid spheres is obtained from the equilibrium statistical mechanics in the virial expansion form

$$p^0 = nkT [1 + bn + 0.6250b^2n^2 + 0.2869b^3n^3 + 0.115b^4n^4 + \dots] \quad (3.27)$$

Thus b has the meaning of the second virial coefficient per molecule, and χ^0 may be expressed in terms of the density expansion as

$$\chi^0 = 1 + 0.6250bn + 0.2869b^2n^2 + 0.115b^3n^3 + \dots \quad (3.28)$$

On the other hand, with use of the perturbation function the thermal energy fluxes, q_k and q_0 , given by (3.14) are expressed in the forms:

$$q_k = \frac{1}{2} m \int V^2 V f^0 \phi dv, \quad (3.29-K)$$

and

$$q_0 = \frac{3}{5} nb\chi^0 q_k + \frac{3kT}{2m} \tilde{\omega} \nabla \frac{1}{T}. \quad (3.29-C)$$

It should be noted that $nb\chi^0$ and $\tilde{\omega}$ in these flux vectors are independent of the molecular distribution.

§ 4. Statistical Expression of the Irreversible Production of Entropy

We shall first consider the equilibrium values of the entropy of an imperfect gas made of rigid spheres. The entropy of an imperfect gas can be given by the form:

$$S^0 = S_{ia}^0 + \frac{\partial}{\partial T} \left\{ \lim_{v_0 \rightarrow \infty} \int_{v_0}^v (p^0 - p_{id}^0) dV \right\}, \quad (4.1)$$

where the subscript "id" denotes a function for the corresponding perfect gas. This equation allows us to calculate the equilibrium value of the entropy S^0 , if we know the equation of state in the form of p^0 as a function of T and volume V . Then we obtain from (3.26) and (4.1), the expression for the entropy per unit volume

$$n\hat{S}^0 = n\hat{S}_{ia}^0 - n \frac{\partial}{\partial T} \left\{ kTb \int^n \chi^0 dn \right\}, \quad (4.2)$$

where we used n instead of V as the independent variable. Since χ^0 is independent of the temperature as seen from (3.28), we obtain

$$n\hat{S}^0 = n\hat{S}_{ia}^0 + n\hat{S}_{\text{corr}}^0, \quad (4.3)$$

$$n\hat{S}_{\text{corr}}^0 = -knb \int^n \chi^0 dn, \quad (4.4)$$

where $\hat{S}_{\text{corr}}^0$ is the correction to entropy per molecule due to the imperfectness of the gas.

On the other hand, the entropy per molecule of an ideal gas composed of point molecules is known to be

$$\hat{S}_{ia}^0 = k \left[-\ln n + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi mk}{h^2} \right) + \frac{5}{2} \right]. \quad (4.5)$$

In fact, according to the H-theorem*, the entropy density of the gas of point molecules is given by

$$n\hat{S}_1 = k \int f(1 - \ln f) dv, \quad (4.6)$$

which becomes identical with (4.5) for the equilibrium distribution $f = f^0$ apart from the constant.

For the present, the system is moderately dense and the correction due to the gas imperfection appear through the χ factor, and furthermore we assume the χ factor to be equal to the equilibrium value χ^0 without

* Usually the entropy is given by $n\hat{S} = -k \int f \ln f dv$, but the expression of the entropy of ideal gas in Bose- and Fermi- statistics becomes identical with (4.6) in classical limit.

appreciable error. Then we may write the entropy density of the imperfect gas out of equilibrium as the sum of (4.6) and (4.4)

$$n\hat{S} = n\hat{S}_1 + n\hat{S}_2, \\ n\hat{S}_2 = n\hat{S}_{\text{corr}}^0 = -knb \int \chi^0 dn. \quad (4.7)$$

Multiplying (2.5) by $k(1 - \ln f)$ and integrating with respect to v , we obtain,

$$\frac{\partial(n\hat{S}_1)}{\partial t} + \nabla \cdot k \int v f (1 - \ln f) dv = k \sum_{i=1}^6 I_i(-\ln f), \quad (4.8)$$

where I_i is given by (3.4). The manner of derivation of (4.8) is similar to that for (3.3), but its third member vanishes in this case. Using the equation of continuity (3.9) we can rewrite (4.8) as

$$n \frac{D\hat{S}_1}{Dt} + \nabla \cdot k \int v f (1 - \ln f) dv = -k \sum_{i=1}^6 I_i(\ln f). \quad (4.9)$$

Since the entropy due to the gas imperfection, $\hat{S}_2$, depends on the spatial coordinates only through the number density n , we can easily obtain

$$n \frac{D\hat{S}_2}{Dt} = kn^2 b \chi^0 \nabla \cdot v_0, \quad (4.10)$$

where we used again the continuity equation for n .

From (3.18) and (3.19), we have

$$\ln f = \ln n - \frac{mV^2}{2kT} - \frac{3}{2} \ln \frac{2\pi kT}{m} + \ln(1 + \phi). \quad (4.11)$$

Substituting the above expression into (4.9), and reminding that $mV^2/2$ is one of the summational invariants, we can write the right-hand side of (4.9), according to (3.4) and (3.5), as follows:

$$\begin{aligned} -k \sum_{i=1}^6 I_i(\ln f) &= -k \left\{ -\nabla \cdot \mathbf{J}_c \left(-\frac{mV^2}{2kT} \right) + \phi \left(-\frac{mV^2}{2kT} \right) \right\} - k \sum_{i=1}^6 I_i(\phi) \\ &= -\nabla \cdot \frac{\mathbf{q}_c}{T} + \mathbf{q}_c \cdot \nabla \frac{1}{T} - \frac{1}{T} \mathbf{P}_c : \nabla v_0 - k \sum_{i=1}^6 I_i(\phi) \end{aligned} \quad (4.12)$$

In the derivation of the above equation, it should be noted that

$$\begin{aligned} \phi \left[-\frac{mV^2}{2kT} \right] &= \frac{1}{k} \left[-\frac{1}{T} \phi \left(\frac{mV^2}{2} \right) - \mathbf{J}_c \left(\frac{mV^2}{2} \right) \cdot \nabla \frac{1}{T} \right] \\ &= \frac{1}{k} \left[\frac{1}{T} \mathbf{P}_c : \nabla v_0 - \mathbf{q}_c \cdot \nabla \frac{1}{T} \right]. \end{aligned}$$

Here we have ignored the terms higher than the square of ϕ , and $\mathbf{q}_c$ and $\mathbf{P}_c$ in (4.12) are given by (3.29-C) and (3.21-C), respectively. To the same approximation $I_i(\phi)$ [cf. (3.4)] are reduced to

$$I_1^0(\phi) = \int \phi J_1^0 dv = -\frac{1}{4} \chi^0 \iiint (\phi' + \phi'_1 - \phi - \phi_1)^2 f^0 f_1^0 \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \quad (4.13-1)$$

$$I_2^0(\phi) = \int \phi J_2^0 dv = \frac{1}{k} \left[\frac{3}{5} nb \chi^0 \mathbf{q}_c \cdot \nabla \frac{1}{T} + \frac{2}{5} nb \chi^0 (\mathbf{P}_c - nkT\mathbf{U}) : \left(-\frac{\nabla v_0}{T} \right) \right], \quad (4.13-2)$$

$$I_3^0(\phi) = \int \phi J_3^0 dv = - \int nb \chi^0 (V \cdot \nabla \ln \chi^0) f^0 \phi dv = 0, \quad (4.13-3)$$

and

$$I_4^0(\phi) = I_5^0(\phi) = I_6^0(\phi) = 0, \quad (4.13-4)$$

where $\mathbf{q}_k$ and $\mathbf{P}_k$ are given by (3.29-K) and (3.21-K), respectively, [cf. Appendix II]. Here I_i^0 and J_j^0 indicate the first approximations to the integrals I_i and J_i , respectively.

From (4.7), (4.9), (4.10) and (4.13), we obtain finally the expression for the entropy balance equation

$$n \frac{D\hat{S}}{Dt} + \nabla \cdot \sigma[s] = \tau^1[s], \quad (4.14)$$

where σ and τ^1 are respectively given by

$$\sigma[s] = k \int V(1 - \ln f) f dv + \frac{q_c}{T} \quad (4.15)$$

and

$$\begin{aligned} \tau^1[s] = & -kI_1^0(\phi) + \left[q_c - \frac{3}{5}nb\chi^0 q_k \right] \cdot \nabla \frac{1}{T} \\ & + \left[P_c - \frac{2}{5}nb\chi^0(P_k - nkT\mathbf{U}) \right] : \left(-\frac{\nabla v_0}{T} \right) \\ & + kn^2b\chi^0 \nabla \cdot v_0. \end{aligned} \quad (4.16)$$

We can immediately see that σ is the entropy flux vector and τ^1 is the irreversible production of entropy per unit volume and unit time.

If we use (4.11) and neglect ϕ^2 in the first member of the right-hand side of (4.15), we immediately obtain from (3.29-K) and (3.14)

$$\sigma = \frac{q_k}{T} + \frac{q_c}{T} = \frac{q}{T}, \quad (4.17)$$

q being the thermal energy flux given by (3.14).

We shall now consider the bracket expression $\{\phi, \phi\}$ defined by the following integral

$$\{\phi, \phi\} = - \iiint \phi(\phi' + \phi'_1 - \phi - \phi_1) f^0 f_1^0 \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \quad (4.18)$$

where ϕ is any function of the molecular velocity $\mathbf{v}$. This bracket expression may be symmetrized by the same arguments as in Appendix I, as

$$\{\phi, \phi\} = \frac{1}{4} \iiint (\phi' + \phi'_1 - \phi - \phi_1)(\phi' + \phi'_1 - \phi - \phi_1) f^0 f_1^0 \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 = \{\phi, \phi\}. \quad (4.19)$$

The operator $\{\}$ is linear, so we have

$$\{\phi + \varphi, \phi\} = \{\phi, \phi\} + \{\varphi, \phi\}, \quad (4.20)$$

and it can easily be shown that

$$\{\phi, \phi\} = \frac{1}{4} \iiint (\phi' + \phi'_1 - \phi - \phi_1)^2 f^0 f_1^0 \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \geq 0, \quad (4.21)$$

Since the integrand can never be negative, $\{\phi, \phi\}$ vanishes if and only if ϕ is a linear combination of the summational invariants.

Consequently, we can obtain from (4.13-1)

$$-kI_1^0(\phi) = k\chi^0 \{\phi, \phi\}. \quad (4.22)$$

Using (3.21), (3.29) and (4.22), we can express (4.16) in the following form:

$$\tau^1[s] = k\chi^0 \{\phi, \phi\} + \frac{3kT}{2m} \tilde{\omega} \left[\nabla \frac{1}{T} \right]^2 + \frac{6}{5} \tilde{\omega} \left[\frac{\mathbf{S}}{T} : \frac{\mathbf{S}}{T} \right] + \tilde{\omega} \left[\frac{\nabla \cdot v_0}{T} \right]^2 \geq 0, \quad (4.23)$$

of which the second, third, and fourth terms are independent of the molecular distribution.

§ 5. The Entropy Production in the Thermodynamics of Irreversible Processes

In the thermodynamics of irreversible processes, the local entropy production is calculated with use of the Gibbs relation, and is given as a function of the thermal energy flux q , the pressure tensor $\mathbf{P}$, $\nabla(1/T)$ and $\nabla v_0/T$:

$$\tau^{II}[s] = q \cdot \nabla \frac{1}{T} + (\mathbf{P} - p^0 \mathbf{U}) : \left(-\frac{\nabla v_0}{T} \right), \quad (5.1)$$

where p^0 is the equilibrium hydrostatic pressure.

In the case of a dense gas of rigid sphere molecules, we may use (3.25) and (3.29) for $\mathbf{P}$ and q , respectively. Then we have

$$\begin{aligned} \tau^{\text{II}}[s] = & \frac{3kT}{2m} \tilde{\omega} \left[\nabla \frac{1}{T} \right]^2 + \frac{6}{5} \tilde{\omega} \left[\frac{\mathbf{S}}{T} : \frac{\mathbf{S}}{T} \right] + \tilde{\omega} \left[\frac{\nabla \cdot \mathbf{v}_0}{T} \right]^2 \\ & + \left[1 + \frac{3}{5} nb\chi^0 \right] q_k \cdot \nabla \frac{1}{T} + \left[1 + \frac{2}{5} nb\chi^0 \right] \\ & \times (\mathbf{P}_k - nkT\mathbf{U}) : \left(-\frac{\nabla \mathbf{v}_0}{T} \right). \end{aligned} \quad (5.2)$$

Here the entropy production must be positive according to the second law of thermodynamics.

If the statistical entropy production given by (4.23) is equal to the thermodynamic entropy production $\tau^{\text{II}}[s]$ obtained from the Gibbs relation, that is $\tau^{\text{I}} = \tau^{\text{II}}$, we have

$$\begin{aligned} & \left[1 + \frac{3}{5} nb\chi^0 \right] q_k \cdot \nabla \frac{1}{T} + \left[1 + \frac{2}{5} nb\chi^0 \right] \\ & \times (\mathbf{P}_k - nkT\mathbf{U}) : \left(-\frac{\nabla \mathbf{v}_0}{T} \right) = k\chi^0 \{ \phi, \phi \}. \end{aligned} \quad (5.3)$$

For convenience we shall write above equation in the following form

$$\int \mathcal{E} f^0 \phi dv = k\chi^0 \{ \phi, \phi \}, \quad (5.4)$$

where

$$\begin{aligned} \mathcal{E} = & \left[1 + \frac{3}{5} nb\chi^0 \right] \frac{mV^2}{2} \nabla \cdot \nabla \frac{1}{T} \\ & + \left[1 + \frac{2}{5} nb\chi^0 \right] m \left(\nabla \nabla - \frac{1}{3} \nabla^2 \mathbf{U} \right) : \left(-\frac{\nabla \mathbf{v}_0}{T} \right). \end{aligned} \quad (5.5)$$

the flux vectors defined by (3.21-K) and (3.29-K) being used.

§ 6. Enskog's First Approximation Solution and Variation Principle for the Modified Boltzmann Equation

If we apply the Chapman-Enskog perturbation method to the modified Boltzmann equation (2.5), we readily obtain Enskog's first approximation equation^{*})

$$\begin{aligned} f^0 \left[\left(1 + \frac{3}{5} nb\chi^0 \right) \left(\frac{mV^2}{2kT} - \frac{5}{2} \right) \nabla \cdot \nabla \ln T \right. \\ \left. + \left(1 + \frac{2}{5} nb\chi^0 \right) m \left(\nabla \nabla - \frac{1}{3} \nabla^2 \mathbf{U} \right) : \left(\frac{\nabla \mathbf{v}_0}{T} \right) \right] \\ = \chi^0 \int \left(\phi^{*'} + \phi_1^{*'} - \phi^* - \phi_1^* \right) f^0 f_1^0 \sigma^2 (g \cdot k) dk dv_1, \end{aligned} \quad (6.1)$$

where the notation ϕ^* is used to be distinguished from an arbitrary perturbation function ϕ in the previous sections.

Then it is quite obvious from (5.5) and (6.1) that Enskog's solution satisfies the relation:

$$\int \mathcal{E} f^0 \phi^* dv = k\chi^0 \{ \phi^*, \phi^* \}. \quad (6.2)$$

This is the same as the condition (5.4), and therefore the solution of (6.1), ϕ^* , is compatible with the Gibbs relation in the irreversible thermodynamics.

If we multiply (6.1) by a trial function ϕ , which satisfies the conditions (3.20) and (5.4), then according to the definition of the bracket notation (4.18), we find

$$\int \mathcal{E} f^0 \phi dv = k\chi^0 \{ \phi, \phi^* \} = k\chi^0 \{ \phi^*, \phi \} = k\chi^0 \{ \phi, \phi \}. \quad (6.3)$$

From the properties of the bracket notation, (4.20) and (4.21), we obtain

$$\begin{aligned} \{ \phi^* - \phi, \phi^* - \phi \} &= \{ \phi^*, \phi^* \} - \{ \phi, \phi^* \} - \{ \phi^*, \phi \} \\ &+ \{ \phi, \phi \} \geq 0. \end{aligned} \quad (6.4)$$

Thus we have the following inequality

$$\{ \phi^*, \phi^* \} \geq \{ \phi, \phi \}. \quad (6.5)$$

This implies that the perturbation ϕ , compatible with the thermodynamic Gibbs relation, maximizes the value of $\{ \phi, \phi \}$ when ϕ is the solution of Enskog's first approximation equation (6.1).

Since in the present variation principle the intensive variables, such as T , $\mathbf{S}$, $\nabla \mathbf{v}_0$ are all prescribed at every point of the space, the last three terms in (4.23) are constant independent of ϕ . Hence the variation principle expressed by (6.5) refers to the maximum of the local entropy production per unit time. Thus we have

$$\tau^{\text{I}}[S] = \text{Maximum}, \quad (6.6)$$

with the condition

$$\tau^{\text{I}}[S] = \tau^{\text{II}}[S]. \quad (6.7)$$

The solution of this variational principle which satisfies the auxiliary conditions (3.20), is determined unambiguously.

This principle can further be rewritten in the equivalent form

$$\tau^{\text{I}}[S] - \frac{1}{2} \tau^{\text{II}}[S] = \text{Maximum}, \quad (6.8)$$

where the variation may be taken as to the perturbation ϕ without the restriction conditions except the simple ones (3.20). This

* For the details of derivation of (6.1), see pp. 276-280 of Chapman and Cowling's book⁵⁾. The zeroth and first approximation in the present paper correspond to the first and the second approximation in Chapman and Cowling's book.

formula seems to be entirely analogous to the thermodynamic variation principle proposed by Onsager⁷⁾.

§ 7. Conclusion

It has been shown that the Enskog's first approximation solution is obtained as the solution of the variation principle. The local entropy production is the maximum for this solution under the condition to satisfy the thermodynamic Gibbs relation. Thus it has been found that the same variation principle as that demonstrated by Ono³⁾ in the case of a dilute gas is preserved also in the case of a dense gas composed of hard sphere molecules, if we add the correction due to the gas imperfection to the entropy.

Consequently, it seems to be possible that, in the linear transport processes well described in the frame of the irreversible thermodynamics based on the Gibbs relation, the most probable distribution function in kinetic theory, compatible with this thermodynamic description, can be obtained by maximization of the local entropy production per unit time under the condition that the Gibbs relation be satisfied. Then, with use of this distri-

bution function the transport coefficients can be calculated. The variational method based on the principle described above seems to be useful to get approximate values of transport coefficients, especially for the case of a dense gas, in which the direct solution of Enskog's first approximation equation is so complicated.

Acknowledgement

The author wishes to express his great gratitude to Prof. Syu One at the University of Tokyo for his invaluable advice and encouragement. A part of this work has been supported by a Grant in Aid for Fundamental Scientific Research from the Ministry of Education.

Appendix I

From (3.4) and (2.4-1), we have

$$\begin{aligned} I_1(\psi) &= \int \psi J_1 dv \\ &= \chi^0 \iiint \phi (f' f_1' - f f_1) \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1. \end{aligned} \quad (\text{A-1})$$

The integral on the right hand side of this equation may be symmetrized by the same argument as in a proof of the H-theorem:

$$\begin{aligned} I_1(\psi) &= -\chi^0 \iiint \phi' (f' f_1' - f f_1) \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \\ &= -\frac{\chi^0}{2} \iiint (\psi' - \psi) (f' f_1' - f f_1) \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \\ &= -\frac{\chi^0}{2} \iiint (\psi_1' - \psi_1) (f' f_1' - f f_1) \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \\ &= -\frac{\chi^0}{2} \iiint (\psi' + \psi_1' - \psi - \psi_1) (f' f_1' - f f_1) \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1. \end{aligned} \quad (\text{A-2})$$

By a similar manipulation it can be shown that

$$\begin{aligned} I_2(\psi) &= \int \psi J_2 dv \\ &= \frac{1}{2} \sigma \chi^0 \iiint [(\psi - \psi') \mathbf{k} \cdot \mathbf{f} \nabla f_1 - (\psi_1 - \psi_1') \mathbf{k} \cdot \mathbf{f}_1 \nabla f] \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \end{aligned} \quad (\text{A-3})$$

$$\begin{aligned} I_3(\psi) &= \int \psi J_3 dv \\ &= -\frac{1}{4} \sigma \iiint (\psi' - \psi_1' - \psi + \psi_1) (\mathbf{k} \cdot \nabla \chi^0) f f_1 \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \end{aligned} \quad (\text{A-4})$$

$$\begin{aligned} I_4(\psi) &= \int \psi J_4 dv \\ &= \frac{1}{4} \sigma^2 \chi^0 \iiint [(\psi' - \psi) \mathbf{k} \mathbf{k} : (f \nabla \nabla f_1) + (\psi_1' - \psi_1) \mathbf{k} \mathbf{k} : (f_1 \nabla \nabla f)] \sigma^2(\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \end{aligned} \quad (\text{A-5})$$

$$\begin{aligned}
 I_5(\phi) &= \int \phi J_5 dv \\
 &= \frac{1}{4} \sigma^2 \iiint [(\phi' - \phi)(\mathbf{k} \cdot \nabla f f_1) + (\phi_1' - \phi_1)(\mathbf{k} \cdot f_1 \nabla f)] (\mathbf{k} \cdot \nabla \chi^0) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \quad (A-6)
 \end{aligned}$$

and

$$\begin{aligned}
 I_6(\phi) &= \int \phi J_6 dv \\
 &= -\frac{1}{16} \sigma^2 \iiint (\phi' + \phi_1' - \phi - \phi_1) (\mathbf{k} \mathbf{k} : \nabla \nabla \chi^0) (f' f_1' - f f_1) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1. \quad (A-7)
 \end{aligned}$$

If ϕ is one of the summational invariants, that is $\phi' + \phi_1' = \phi + \phi_1$, then it can be immediately seen that

$$\begin{aligned}
 I_1(\phi) &= 0, \\
 I_2(\phi) &= -\frac{\sigma}{2} \chi^0 \iiint (\phi' - \phi) \{ \mathbf{k} \cdot \nabla (f f_1) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \\
 I_3(\phi) &= -\frac{\sigma}{2} \iiint (\phi' - \phi) (\mathbf{k} \cdot \nabla \chi^0) f f_1 \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \\
 I_4(\phi) &= \frac{\sigma^2}{4} \chi^0 \iiint (\phi' - \phi) \left[\mathbf{k} \mathbf{k} : \nabla \left(f f_1 \nabla \ln \frac{f_1}{f} \right) \right] \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \\
 I_5(\phi) &= \frac{\sigma^2}{4} \chi^0 \iiint (\phi' - \phi) \left\{ \mathbf{k} \cdot f f_1 \nabla \ln \frac{f_1}{f} \right\} (\mathbf{g} \cdot \nabla \chi^0) \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1,
 \end{aligned}$$

and

$$I_6(\phi) = 0.$$

Consequently, we have

$$\begin{aligned}
 I_2(\phi) + I_3(\phi) &= -\nabla \cdot \left[\frac{\sigma}{2} \iiint (\phi' - \phi) \chi^0 f f_1 \mathbf{k} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \right] \\
 &\quad + \frac{\sigma}{2} \iiint \chi^0 f f_1 \{ \mathbf{k} \cdot \nabla (\phi' - \phi) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) \mathbf{g} d\mathbf{k} dv dv_1 \quad (A-8)
 \end{aligned}$$

and

$$\begin{aligned}
 I_4(\phi) + I_5(\phi) &= -\nabla \cdot \left[\frac{\sigma^2}{4} \iiint (\phi' - \phi) \mathbf{k} \chi^0 f f_1 \left\{ \mathbf{k} \cdot \nabla \ln \frac{f_1}{f} \right\} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \right. \\
 &\quad \left. + \frac{\sigma^2}{4} \iiint \chi^0 f f_1 \left\{ \mathbf{k} \cdot \nabla \ln \frac{f_1}{f} \right\} \{ \mathbf{k} \cdot \nabla (\phi' - \phi) \} \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1 \right]. \quad (A-9)
 \end{aligned}$$

Thus we have the expressions (3.5), (3.6) and (3.7) for the summational invariants ϕ .

Appendix II

The integral $I_i(\phi)$ is given by

$$I_i(\phi) = \int J_i \phi dv \quad (i=1, 2, 3, 4, 5, 6), \quad (A-10)$$

where J_i is defined by (2.4). Throughout the present treatment the perturbation function ϕ and the space derivatives of n , v_0 , T are considered to be small quantities. Substituting $f = f^0(1 + \phi)$ into J_i , and retaining only the first order perturbation, we get the following expressions for J_i .

Neglecting the square terms of ϕ in J_1 , we have

$$J_1^0 = \chi^0 \iint (\phi' + \phi_1' - \phi - \phi_1) f^0 f_1^0 \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv_1$$

as the first approximation to J_1 . Hereafter we shall denote the first approximation to J_i by J_i^0 .

Since J_2 and J_3 themselves involve the derivatives of the macroscopic variables, then we may neglect all the terms involving ϕ , and write f^0 instead of f in these J_i . Then, performing the integration of the terms J_2^0 and J_3^0 , we obtain the following results:

$$J_2^0 = -nb\chi^0 \left[\mathbf{V} \cdot \left\{ 2\nabla \ln n + \left(\frac{3}{10} \frac{mV^2}{kT} - \frac{1}{2} \right) \nabla \ln T \right\} + \frac{2}{5} \frac{m}{kT} \mathbf{V} \mathbf{V} : \nabla \mathbf{v}_0 - \left(1 - \frac{mV^2}{5kT} \right) \nabla \cdot \mathbf{v}_0 \right] f^0, \quad (\text{A-11})$$

$$J_3^0 = -nb\chi^0 (\mathbf{V} \cdot \nabla \ln \chi^0) f^0. \quad (\text{A-12})$$

Finally, J_4, J_5, J_6 are all zero in this approximation, since they involve the second derivatives of the macroscopic variables or squares of the first derivatives:

$$J_4^0 = J_5^0 = J_6^0 = 0. \quad (\text{A-13})$$

Replacing J_i in (A-10) by J_i^0 , we obtain

$$\begin{aligned} I_1^0(\phi) &= \chi^0 \iiint \phi (\phi' + \phi_1' - \phi - \phi_1) f^0 f_1^0 \sigma^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} dv dv_1, \\ I_2^0(\phi) &= \frac{1}{k} nb\chi^0 \left[\frac{3}{5} \nabla \frac{1}{T} \cdot \int \frac{mV^2}{2} \mathbf{V} f^0 \phi dv - \frac{2}{5} \frac{\nabla \mathbf{v}_0}{T} : \int m \mathbf{V} \mathbf{V} f^0 \phi dv \right], \\ I_3^0(\phi) &= -nb\chi^0 \int (\mathbf{V} \cdot \nabla \ln \chi^0) f^0 \phi dv = 0, \end{aligned}$$

and

$$I_4^0(\phi) = I_5^0(\phi) = I_6^0(\phi) = 0.$$

References

- 1) E. J. Hellund and E. A. Uehling: *Phys. Rev.* **56** (1939) 818.
- 2) C. F. Curtiss and J. O. Hirschfelder: *J. Chem. Phys.* **17** (1949) 550.
- 3) S. Ono: *Scientific Papers of the College of General Education, University of Tokyo* **5** (1955) 87.
- 4) D. Enskog: *K. Svenska Vetenskaps Akademiens Handle.* **63** (1921) no. 4.
- 5) S. Chapman and T. G. Cowling: *The Mathematical Theory of Non Uniform Gas.* (Cambridge Univ. Press, 1939).
- 6) J. O. Hirschfelder, C. F. Curtiss and R. N. Bird: *Molecular Theory of Gases and Liquids* (New York, 1954).
- 7.) L. Onsager: *Phys. Rev.* **37** (1931) 405.

Dislocation Model of Liquid Structure

By Sanchi MIZUSHIMA

Faculty of Engineering, Keio University, Tokyo

(Received May 19, 1958)

Liquid structure can be considered as a lattice distorted heavily by many dislocation lines. The dislocation density is supposed to be limited by the mutual contact of the cores of the dislocation lines. Calculation of the free energy as function of the dislocation density showed that above a certain temperature the lattice which has no dislocations at low temperatures changes abruptly into liquid by the appearance of the highest density of dislocations. Calculated heat of fusion of various metals agrees fairly well with experiment if the core radius is taken to be of the order of the lattice constant. In this model the thermal expansion of the liquids can be explained just in the same way as that of solids. A method of calculation was applied to determine the Grüneisen constant of molecular liquids with the result confirming this model.

§ 1. Introduction

Models of liquid structure which have been used frequently to explain the properties of liquids are, 1) method of free volume¹⁾, 2) method of lattice gas with interstitial sublattices²⁾, 3) hole theory³⁾ 4) to regard the liquid as an aggregate of crystallites⁴⁾ etc. Though each of them has its own feature, it does not seem that the mechanism of melting has been made clear quantitatively enough. Theories proposed up to now are either so idealized that the comparison with experiment is not easy or is showing only the instability of solid lattice above a certain temperature.

The most characteristic property of liquid as compared with solid is of course its fluidity. Even when a substance has a number of different phases, what is called liquid phase among condensed phases is that which is fluid. Hole theories attempt to explain the fluidity by the migration of lattice vacancies, but it is easy to show that such vacancies as assumed in ordinary treatment never make such convenient migration under shear stress to give shear flow. Eyring's theory of the viscosity of liquid cannot be justified if taken in its strict sense. Therefore, a lattice containing vacancies remains to be solid always. In order to explain the fluidity any model of liquid structure, if it is going to make use of a lattice-like arrangement of molecules, should consider dislocations.

The model of liquid structure treated in this paper is based upon the observation that the liquid is crystal-like in short range but

has no long range order. The molecules are considered to take lattice-like arrangement which, however, is saturated by many dislocation lines, or in other words, is distorted by the highest density of dislocations. In the following sections it will be shown that the melting of solid can be explained by the sudden appearance of dislocations in a perfect lattice and that this phase transition is always accompanied by the latent heat of fusion.

§ 2. Dislocation Network

We wish to form a dislocation network in a monatomic lattice of one gram atom. Let the lattice be simple cubic, and its lattice constant be a , which is fixed to a certain value simply, irrespective of the dislocation density. For the sake of simplicity the density of dislocations is considered to be uniform throughout the lattice. Now, by calculating the excess free energy of the lattice due to the presence of dislocations as function of the dislocation density ρ it will be shown that when the temperature is below a certain temperature T_f the state of perfect lattice where $\rho=0$ is the most stable one, and on the other hand when the temperature is above T_f the state of the highest disorder where $\rho=\rho_{\max}$ is the most stable one. The transition temperature T_f should then correspond to the melting temperature, and the state of the disordered lattice to the liquid state.

The lattice is divided into a number of cubic domains of equal volume. The size of a domain is variable, while the lattice constant

is fixed. Each domain is given a line element of dislocation. Therefore, when the dislocation density is specified, the volume of a domain is determined which, however, cannot be excessively small because of the necessity to contain a dislocation line element. The direction of a line element is assumed to be parallel to one of the three [100] axes. In case neighboring domains have their line elements passing through their common domain boundary, these two elements are regarded to form one dislocation branch. If the boundary between neighboring domains is passed only by one line element of either domain, we regard the other domain to have a node at its center and the former line element or branch is extended up to here. A branch, which is always straight, may be composed of one, two or more line elements. Some domains have nodes and others have not. A node may be associated with from 3, the minimum number, to 6, the maximum number, branches. In this way we obtain a complete configuration of the dislocation network except that the Burgers vector of each branch is not defined yet. Fig. 1 shows an example of the way the line elements are connected with others to form branches and nodes. By chang-

ing the directions of the elements we can compose other configurations of the network.

Quantities needed for the calculation of the free energy F as function of the dislocation density ρ are as follows.

- Dislocation line density (total length of the lines per unit volume of the lattice) $\dots \rho$
- Edge length of a domain $\dots \rho^{-1/2}$
- Number of atoms in a domain $\dots \rho^{-3/2}a^{-3}$
- Total number of domains in the lattice $\dots$
 $\dots n = N_0 a^3 \rho^{3/2}$
- Total length of the dislocation lines $\dots$
 $\dots N_0 a^3 \rho$

Here N_0 is the Avogadro number. The extension of the line elements of branches mentioned above becomes necessary very often to complete the connection of all branches as seen in Fig. 1. Contribution from such extensions is neglected for simplicity, however, since it does not change much the following calculation even if taken into account.

§ 3. Energy due to Dislocations

The increase of energy E due to the presence of dislocations is calculated as follows. Energy per atomic plane, $\mathcal{E}$, is divided as usual into two parts, $\mathcal{E}_{\text{core}}$, which is the contribution from the dislocation core, and $\mathcal{E}_{\text{elas}}$, which is the elastic deformation energy of the lattice surrounding the core.

$$\mathcal{E} = \mathcal{E}_{\text{core}} + \mathcal{E}_{\text{elas}}.$$

$\mathcal{E}_{\text{elas}}$ depends logarithmically on the ratio of the mean distance between the lines to the radius of the core, r_0 , where the cross-section of a core is assumed to be a circle.

$$\mathcal{E}_{\text{elas}} = (1/4\pi) G_0 a^3 \ln (\rho^{-1/2} / \pi^{1/2} r_0). \quad (1)$$

Here the distance between the lines is approximated by the edge length of a domain, $\rho^{-1/2}$, and the absolute value of the Burgers vector is taken as equal to the lattice constant a . The difference due to type of dislocation is neglected. The form of this expression is so chosen as to make $\mathcal{E}_{\text{elas}}$ zero when the area of one of the domain walls ρ^{-1} is equal to the cross-section of the core πr_0^2 . G_0 is the modulus of rigidity of the lattice. The effect of the value of the Poisson's ratio is neglected for simplicity.

On the other hand, the core energy is rather difficult to treat theoretically. We wish to define the core size to be such that its di-

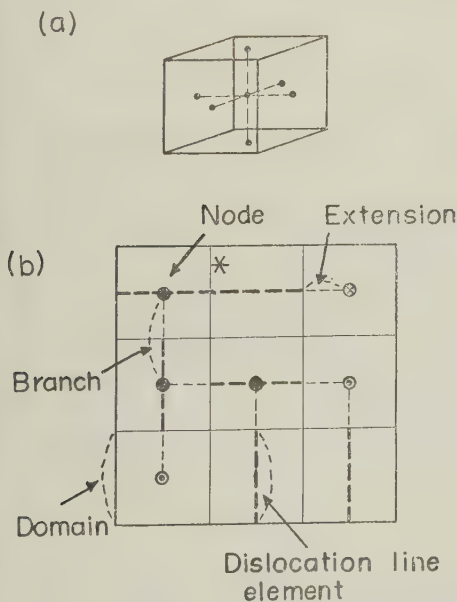


Fig. 1. (a) A domain showing three possible directions of the dislocation line element.

(b) Branches and nodes of the dislocation network formed by connecting the line elements in different domains.

ameter represents the minimum distance of approach of neighboring dislocation line elements without destroying the "dislocation structure" of themselves, and suppose here a core is made of only several atoms per atomic plane, judging from the experiment of Fukushima and Ookawa on the grain boundaries in two-dimensional soap bubble raft⁶⁾.

Recently Mandurin calculated the strain energy of a screw dislocation line in a cylinder of radius R^0 . For a certain configuration of the dislocation in a simple cubic lattice, he found that the energy per unit length is given by:

$$(1/4\pi)G_m b^2 \ln(R/r').$$

Here G_m is the geometrical mean of two macroscopic elastic coefficients, b the Burgers vector and r' a length which depends on the lattice constant and slightly on the ratio of the two elastic coefficients. r' is much smaller than the lattice constant. If we introduce a radius of core r_0 , which he did not need to make use of, the above expression can be divided into the core and the "elastic" part as

$$(1/4\pi)G_m b^2 \{\ln(r_0/r') + \ln(R/r_0)\}.$$

This expression of the core energy, when transferred to our case, will give for the core energy *per atomic plane* the following equation.

$$\varepsilon_{\text{core}} = \{\ln(r_0/r')/4\pi\} G_m a^3.$$

Because his calculation is based upon the assumption that each atom interacts with its neighbor through Hooke's law force, this equation cannot be expected to give a good approximation. Some other laws of force should be applied to determine the interactions among atoms contained in the core. Nevertheless, it does not seem very unreasonable to expect that even such forces not obeying Hooke's law due to the large displacement will be closely related to the macroscopic elastic coefficients.

For this reason we will make use of some kind of modulus of rigidity, denoted as G , for the expression of the core energy per atomic plane and write

$$\varepsilon_{\text{core}} = \alpha G a^3, \quad (2)$$

ignoring that this expression is not so appropriate for edge dislocations as for screw ones. α is considered to be a fraction of unity when

the core radius is taken to be of the order of the lattice constant a .

Thus the total energy E becomes

$$E = N_0 a^5 \rho \{G\alpha - (1/8\pi)G_0 \ln(\pi \rho r_0^2)\}. \quad (3)$$

If the random arrangement of atoms in liquids is to be described by a lattice distorted by dislocations, it is most natural to consider the upper limit of ρ to be the one at which the lattice is filled with the cores, so that

$$\rho_{\text{max}}^{-1/2} = \pi^{1/2} r_0. \quad (4)$$

Corresponding energy, written as E_{max} is

$$E_{\text{max}} = (\alpha/\pi)(a/r_0)^2 G V_0; \quad V_0 = N_0 a^3, \quad (5)$$

which is purely core energy. We will assume later that the radius of the core is equal to the lattice constant for the purpose of simplifying the calculation, though a little larger radius should be more reasonable.

§ 4. Entropy due to Dislocations

The increase of entropy, designated as S , is composed of two parts; the one is that part which can be calculated as $k \ln P$ where P is the number of configurations of the dislocation network at some given dislocation density, and the other is that part due to the decrease of the frequencies of the atomic vibrations.

$$S = S_{\text{config}} + S_{\text{vib}}.$$

(1) Number of configurations of the dislocation network

First we calculate the number of the dislocation line branches. This differs from the total number of the domains, n . Since when neighboring line elements coalesce into a single line we get only one branch instead of two, we have to subtract from n the number of such connections. The probability that a boundary between neighboring domains is passed through by the two line elements at the same time is $(1/3)^2$. As the total number of the boundaries is $3n$, the expectation value of the number of such connections is $n/3$, and the total number of the branches will become $(2/3)n$. But, in addition to this, we have to take into consideration that if a domain has a node in it the number of the branches increases by one, because the line element in that domain is divided into two lines at the node and we shall get two branches instead of one. So we have to add the total number of nodes, ν , to the above figure. Thus the

total number of branches written as B , becomes

$$B = (2/3)n + \nu,$$

where the terms on the right side will be considered to represent the most probable values respectively, and the same thing for the left side.

In the case of Fig. 1 the relation among these numbers is as follows. The number of domains (or line elements) is 9. The number of boundaries which are passed through by two line elements from both sides is 1, marked by * in the figure. The number of nodes is 6, and the total number of branches is 14, which is equal to 9 minus 1 plus 6. Here 6 branches are perpendicular to the sheet, half upward and half downward.

Considering that we have chosen as our lattice a simple cubic lattice, we want to use the following 26 Burgers vectors to determine the number of configurations.

$a[100]$ type ... 6 in all,

$a[110]$ type ... 12 in all,

$a[111]$ type ... 8 in all.

The absolute value of the Burgers vector is different from a , the lattice constant, for the last two types. We will take this into account by interpreting the equation (2) as expressing the mean value of the core energy per atomic plane, and expecting somewhat large value of α .

To determine the physical state of a branch, the direction of each branch has to be specified too. The freedom of this selection is two for each branch. But since, by simultaneous inversion of the Burgers vector and changing of the direction of the branch we obtain the same physical state, the number of different states of a dislocation of a branch is again 26.

Therefore, if there were no restrictions to be taken into account, the number of configurations of the network, denoted as P , would be

$$P = \sum_{i=1}^{3^n} 26^{B_i},$$

where B_i is the number of branches for a given configuration of the line elements, and the summation is over 3^n configurations of the n line elements, considering that the freedom of the direction of each dislocation line element in a domain is 3. We want to simplify this equation by taking the most proba-

ble value of B_i , which will be written as B , and assume

$$P = 3^n \times 26^B,$$

though this expression of P will give a little smaller value of entropy rather than when the original expression is used.

But actually, because of the condition that the vector sum of the Burgers vectors of the branches meeting at a common node must satisfy the Kirchhoff's law, we have to replace B in the above equation by B minus the number of the nodes ν , that is $B - \nu = (2/3)n$. Then,

$$P = 3^n \times 26^{(2/3)n}.$$

Further we have to consider that the number of the ways of the combinations of the Burgers vectors at each node is still more limited because of geometrical reason. For example, the number of possible combinations of the Burgers vectors of three branches meeting at a node is not $26^3 = 676$, where the exponent of the left hand side is the number of the branches minus the number of the above-mentioned conditions, that is, three minus one. Among the various combinations of the Burgers vectors of the free two branches, such ones as $a[100]$ and $a[100]$ are prohibited because the third branch cannot take either the vector $a[200]$ or the vector $a[\bar{2}00]$, while such ones as the combinations $a[100]$ and $a[010]$ are allowed. In case of three branches meeting at a node the number of possible combinations is 264 in reality. If this number is factorized between the free two branches the value of $264^{1/2} \simeq 16.3$ is obtained for one free branch. Approximate calculation shows that nearly the same figure can be applied to every node associated with arbitrary number of branches. Thus we obtain finally

$$P = 3^n \times 16.3^{(2/3)n} = C^n; \quad C \simeq 20.$$

Then S_{config} can be written as

$$S_{\text{config}} = k \ln P = a^3 \rho^{3/2} R \ln C, \quad (6)$$

where R is the gas constant. This quantity increases with ρ , reaching maximum when $\rho = \rho_{\text{max}}$.

(2) Vibrational entropy

We assume that when the lattice is perfect all atoms vibrate with the same frequency f in three directions, while in the presence of dislocations the atoms contained in the dislocation cores change their frequency of the

modes polarized in the direction parallel to the Burgers vector from f to f' , as this direction is the easiest direction for atoms to change positions, while the atoms not contained in the cores do not change their frequency. f' is assumed to be a constant independent of the dislocation density. The ratio f/f' can be expressed approximately as follows. The frequency f for the perfect lattice can be written, since each atom is surrounded by six neighboring atoms in a cubic lattice, roughly as:

$$(2\pi f)^2 m = 2K + 4K'; \quad K, K' > 0,$$

where m is the mass of an atom, K and K' are spring constants for the change of the atomic distance and that of the valency angle respectively. For the vibrational mode of an atom belonging to the core, which is polarized in the direction parallel to the Burgers vector, the form of the contribution to the potential energy from the side of the center of the line changes as

$$(K'/2)x^2 \rightarrow -(K''/2)x^2; \quad K'' > 0,$$

where x is the displacement of the atom from its equilibrium position, and in the right side such terms are omitted which are constant or linear to x , since they do not affect the frequency. The value of K'' will differ among atoms, being large for those near the center of the line, so that we will take its mean value. From this we obtain

$$(2\pi f')^2 m = 2K + 3K' - K''.$$

Now if we let tentatively

$$K \simeq K' \simeq K''/2,$$

then

$$f/f' \simeq 2^{1/2}.$$

The vibrational entropy of the perfect lattice is at temperature T

$$3R \ln(kT/hf),$$

where it is assumed that $T \gg hf/k$. If we measure the entropy of our lattice with the above value as the standard the excess entropy S_{vib} becomes the following, since the total length of the dislocation lines divided by the lattice constant, that is, the total number of atomic planes passed through by all branches, is $a^2 \rho N_0$,

$$S_{\text{vib}} = pa^2 \rho R \ln(f/f'), \quad (7)$$

where p is the number of atoms belonging to the core per atomic plane. Thus the vibra-

tional entropy increases linearly with the dislocation density, a natural result from that the number of atoms vibrating with f' in one of the three directions increases linearly with the total length of the dislocation lines. This entropy reaches maximum when $\rho = \rho_{\text{max}}$, as

$$S_{\text{vib, max}} = R \ln(f/f'), \quad (8)$$

where p in (7) was taken to be equal to $\pi(r_0/a)^2$. In this case all atoms are contained in cores.

§ 5. Free Energy due to Dislocations and the Melting of Solid

From the above calculations the free energy F can be expressed as function of the dislocation density ρ as follows

$$F = V_0 a^2 \rho \{ \alpha G - (1/8\pi) G_0 \ln(\pi \rho r_0^2) \} - RT \{ a^3 \rho^{3/2} \ln C + pa^2 \rho \ln(f/f') \}. \quad (9)$$

The dependency of F upon ρ is shown in Fig. 2 with temperature as parameter. The three curves correspond to different temperatures respectively. Some appropriate values were used for the coefficients in (9) to draw these curves. As can be seen in the figure,

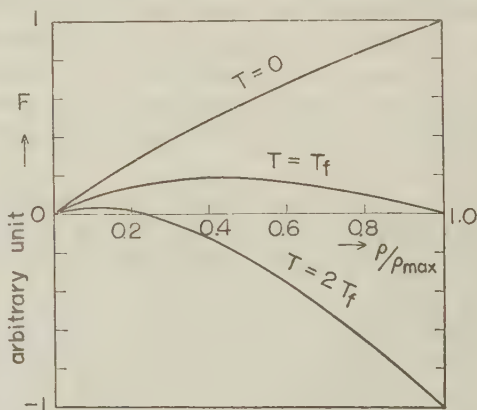


Fig. 2. Free energy F vs. dislocation density ρ at three temperatures. Constants used in drawing the figure are the same as those used to obtain Eq. (11) from (10), and G is assumed to be equal to G_0 .

when $T < T_f$ the free energy becomes minimum (zero) at $\rho = 0$ and when $T > T_f$ at $\rho = \rho_{\text{max}}$, where T_f is a temperature to be determined by letting $\rho = \rho_{\text{max}}$ and $F = 0$ in (9). This feature of F as function of ρ remains unchanged even when other values were used for the coefficients as can be seen easily from

the dependency of F , showing that this transition is common to all lattices.

Accordingly it is concluded that when $T < T_f$ the state of the perfect lattice is the most stable phase which should correspond to solid, and when $T > T_f$ the state of $\rho = \rho_{\max}$ is the most stable one which should correspond to liquid. T_f is then to be regarded to express the melting temperature, and the energy and the entropy associated with this transition are the latent heat of fusion L_f and the entropy of fusion S_f respectively. Thus

$$\begin{aligned} L_f &= (\alpha/\pi)(a/r_0)^2 G V_0, \\ S_f &= \{\pi^{-3/2}(a/r_0)^3 \ln C + \ln(f/f')\} R, \\ T_f &= L_f/S_f. \end{aligned} \quad (10)$$

In order to compare this result with experiment we assume that the radius of the core r_0 is equal to the lattice constant a , and $\alpha/\pi = 0.050$, and take the values calculated above for C and f/f' , that is, 20 and $2^{1/2}$ respectively. From this we obtain

$$\begin{aligned} L_f &= 0.050 G V_0, \\ S_f &= \{1.08(\text{Config}) + 0.69(\text{Vib})\} \text{E.U.} \\ &= 1.77 \text{E.U.} \end{aligned} \quad (11)$$

The value of α/π was so chosen as to give the best agreement between the theoretical heat of fusion and the experimental value for various metals. This value of α , which is about 0.157, seems to be a little smaller than expected, especially when we remind that the absolute value of the Burgers vector was not always restricted to be the same as the lattice constant in § 4. It should be more reasonable to take a somewhat larger value of the core radius, say $1.5a$, and make α be about 0.35. This change would cause the decrease of the configurational entropy. But in our present calculation we want to content ourselves by taking the above simple figures for the sake of simplicity.

As for the entropy of fusion S_f discussions will be given later.

§ 6. Heat and Entropy of Fusion

As is shown in the preceding section the heat of fusion is determined by the modulus of rigidity G . In order to compare our result with experiment we will express the rigidity as function of the elastic coefficients of the lattice. Because the model we are discussing is a cubic lattice, there are three independent elastic coefficients, which are:

$$c_{11}, c_{12}, c_{44}.$$

From these coefficients we can construct the following three different rigidities, G' , G'' and G''' .

$$\begin{aligned} G' &= c_{44}, \\ G'' &= (c_{11} - c_{12})/2, \\ G''' &= 3c_{44}(c_{11} - c_{12})/(4c_{44} + c_{11} - c_{12}). \end{aligned}$$

Here G' is the rigidity which is for the shear stress along (100) plane in the [010] direction, G'' is that for the shear stress along (110) plane in the [110] direction and G''' is that for the shear stress along (111) plane in the [211] direction. We will not consider rigidities for the shear stress along other planes, as the above three sets of planes are the most important glide planes. Now, because the number of the planes (100), that of (110) and that of (111), passing the atoms respectively, contained in the lattice are in the ratio of 6:12:8, the following weighted mean value of the rigidities will be used.

$$G_{\text{mean}} = (3G' + 6G'' + 4G''')/13. \quad (12)$$

Thus equation (11) becomes

$$L_f = 0.050 G_{\text{mean}} V_0. \quad (13)$$

Assuming that this equation holds independent of the crystalline system of real crystals we will compare in Table I the theoretical heat of fusion, which was calculated from the elastic coefficients c_{ij} and the atomic volume V_0 , with experimental value of various metals. Constants needed for calculation were taken from the American Institute of Physics Handbook (1957). As the elastic coefficients are for the room temperature the theoretical heat

Table I. Heat of Fusion of Metals.

	Na	K	Cu	Ag	Au	Al	Si	Ge	Pb	Fe	Ni	W
L_f (calc.)	0.22	0.23	1.34	1.19	1.18	1.16	3.5	3.3	0.60	2.4	2.0	7.2
L_f (meas.)	0.26	0.23	1.30	1.13	1.27	1.09	4.6	3.5	0.48	1.5	1.8	—

in units of 10^{11} erg/mol

at the melting temperature should be a little smaller than the tabulated value, though the increase of V_0 cancels the decrease of c_{ij} to some extent. The agreement between both columns is fairly good, however.

As for the entropy of fusion S_f it is known well that experimental value of many monatomic solids is nearly 2 E.U., agreeing very roughly with the value given in the preceding section tentatively as 1.76 E.U. This value should be lowered if the core radius is taken to be larger than the lattice constant, as said before, because of the decrease of the configurational entropy. But since S_f must depend strongly upon the way the vibrational frequency of atoms changes when contained in the dislocation cores, it is difficult to predict its exact value. For example, measured values of S_f for Si and Ge are as high as of the order of 6.5 E.U., indicating that a large decrease of the frequency occurs when the lattice is distorted by dislocations, even though these solids contract upon fusion, apart from the problem of the configurational entropy. By the way, the contraction of these valence crystals seems to favor our model of liquid structure. Hole theory of melting on the other hand is perhaps not suited to treat such cases.

§ 7. Thermal Expansion of Liquids

In this paper the liquid structure is regarded to form a lattice distorted by the maximum dislocation density. Therefore, if the number of configurations of the dislocation network at the highest density of dislocations does not change with temperature, for which the constancy of the core radius is the first necessary condition, the thermal expansion of a liquid is caused merely because of the decrease of the vibrational frequency of atoms with the increase of the volume of the lattice. This situation seems to hold for simple metals and non-associated liquids at least at temperatures near melting temperatures as shown below. At such temperatures the expansion due to the increase of the number of holes will not make much contribution. On the other hand, associated liquids do not seem to do such simple thermal expansion. According to the author's opinion associated liquids are characterized by that the dislocation cores change their radius with temperature, which would

correspond to the generally accepted theory that the hydrogen bonds break up gradually with the rise of temperature in these liquids.

If all vibrational modes in the lattice change their frequencies in the same manner with the change of the volume of the lattice, the derivative of the entropy of the lattice against the volume can be written as

$$(\partial S / \partial V)_T = -(C_V / V_0) (d \ln f / d \ln V_0),$$

where C_V is the atomic heat at constant volume and V_0 is the atomic volume. Combining this with the thermodynamical equation $(\partial S / \partial V)_T = \alpha_T / \chi$ we obtain the well known Grüneisen formula

$$\alpha_T = \gamma C_V \chi / V_0 \quad (14)$$

where α_T is the thermal expansion coefficient and χ is the compressibility, and

$$\gamma = -d \ln f / d \ln V_0,$$

which is a dimensionless number. The Grüneisen's constant γ is of the order of two for various solid metals, changing very slightly with temperature. Theoretically γ is nearly equal to $(n+2)/6$ when the repulsive potential between neighboring atoms is of the r^{-n} type, where r is the distance between them. If for example n is 10, γ will be two.

For liquid metals it has been shown experimentally⁷⁾ that the value of γ determined from the thermal expansion coefficient and the compressibility agrees closely with that of the corresponding solid metal. This fact favors our model.

For molecular liquids, however, a little different expression of the Grüneisen's formula has to be applied. Among the vibrational modes of a molecule participating in the molecular heat there are three modes of the translational vibration of the center of mass of the molecule, three modes of the rotatory oscillation of the molecule around its axes of moment of inertia, and a number of intramolecular vibrational modes. If the molecule is linear the number of the rotatory oscillations is only two. It will be a good approximation to consider that only the former six or five modes change their frequencies in the same way with the volume of the lattice, while the latter intramolecular vibrations keep their frequencies constant. As the characteristic temperature of the intermolecular vibrations is usually much lower than the room temperature, the molecular heat at constant

Table II. Grüneisen's Constant of Liquids

	CS ₂	CCl ₄	CHCl ₃	Acetone	Ether	Benzene	Toluene	Aniline
γ	1.87	2.22	1.99	1.72	1.82	2.22	2.53	3.40

volume entering our question is either $5R$ or $6R$ depending upon whether the molecule is linear or not, where R is the gas constant. From this we obtain in place of (14),

$$\alpha_T = (\gamma R \chi / V_0) \times \begin{cases} 3 \cdots \text{monatomic molecule} \\ 5 \cdots \text{linear molecule} \\ 6 \cdots \text{multiatomic molecule.} \end{cases}$$

(15)

Using this equation we can determine γ by the measurement of α_T , χ and V_0 .

In Table II are given the values of the Grüneisen's constant of several organic liquids determined by (15) from the thermal expansion coefficient and the compressibility. The constants used in the calculation were taken from the American Institute of Physics Handbook and the Tables of Physical Constants (in Japanese) by K. Shiba. They are for 20°C. The value of γ obtained thus lies in the range from about 2 to 3, showing that the repulsive potential between neighboring molecules obeys roughly the inverse 12th power law, though, of course, this potential is not a very good one for large molecules.

§ 8. Summary and Discussions

The structure of liquids was approximated by a lattice distorted by the highest density of dislocations, or in other words, by a lattice composed entirely of dislocation cores. By assuming the core radius to be of the order of the lattice constant the heat of fusion was expressed as function of three elastic coefficients of cubic lattice. Experimental values of the heat of fusion of various metals agree fairly well with the calculated values if our expression is assumed to hold independent of

crystal structure.

As for the entropy of fusion it is not yet possible to predict its exact value for real substances. Tentative calculation suggested that for monatomic substances about 1 E.U. is of the configurational and the remaining, about 1 E.U. for example, is of the vibrational origin.

The thermal expansion of liquids was explained on this model as only due due to the decrease of the vibrational frequency of atoms or molecules with the increase of the volume of the lattice. Grüneisen's constant was calculated from physical constants for several organic liquids, the result being advantageous to our model.

The concept of lattice vacancies is not included in this paper for the sake of simplicity, because the properties of liquids treated in this paper are easily explained merely by the introduction of the dislocations as shown in the text, though at temperatures far above the melting point the concept of lattice vacancies is useful.

References

1) See J. O. Hirschfelder, C. F. Curtiss and R. B. Bird: *Molecular Theory of Fluids*, 1954 (Wiley).

2) I. Shimose: J. Phys. Soc. Japan **10** (1955) 860.

3) T. Kurosawa: J. Phys. Soc. Japan **12** (1957) 338.

4) A. Ookawa: J. Phys. Soc. Japan **2** (1947) 108.

5) E. Fukushima and A. Ookawa: J. Phys. Soc. Japan **12** (1957) 139.

6) A. A. Maradudin: J. Phys. Chem. Solids **9** (1959) 1.

7) O. J. Kleppa: J. Chem. Phys. **18** (1950) 1331.

Approach to Equilibrium of A Large Fermion System

By Kyoji NISHIKAWA

*Institute of Physics, College of General Education, University of Tokyo,
Tokyo, Japan*

(Received September 5, 1959)

Using Feynman diagrams, the dissipative behaviour of a large quantum system of many fermions is discussed. On the basis of linked cluster expansion of the time-dependent perturbation theory, the master equation is derived for the time sufficiently long compared to the effective collision time and for a slowly varying initial distribution in the momentum space. Van Hove's result for weak coupling limit and the equation for low density limit are obtained as special cases.

§ 1. Introduction

An excellent general analysis of the dissipative behaviour for a large quantum system was made by Van Hove.¹⁾ It was made clear that whether the system behaves dissipative or not is entirely determined by the location of poles of the resolvent

$$[R(l) = 1/(H - l)]$$

where H is the total hamiltonian of the system.

In the present article, we shall make an attempt to study the approach to equilibrium for the case of a system of many fermions which are interacting by two-body potential without external fields. Although our standpoint is in many respects similar to Van Hove's one, the present theory is based on a slightly different method from his.

We use Feynman diagram methods²⁾ which are familiar in the quantum field theory. Especially the expansion in terms of linked clusters is useful for studying the long time behaviour of the von Neumann equation for the time evolution of the density matrix. As is well known, for a large system, the contribution of each linked diagram is proportional to the volume. Then one of the most advantageous points of our theory is that transition to limiting cases, such as weak coupling limit or low density limit, is easily performed, since in these limits the linked diagrams can be classified according to the order of magnitude of their contributions and the most divergent terms can be put together in forms of convergent series. Since Wick's theorem,³⁾ which seems to be essential to our diagram techniques, is not applicable to boson systems in its usual form, we confine our dis-

cussions for the present to fermion systems. However, the same method will be applicable to some other systems, such as an electron phonon system.

The postulate of random a priori phases⁴⁾ is employed for the initial setting of the ensemble and then only spatially homogeneous systems are dealt with.⁵⁾ The extension of our diagram techniques to systems which are inhomogeneous to some extent seems to be possible.

In §2, we give a brief description of the system dealt with in this article. Our starting equation is the von Neumann equation for the density matrix in the interaction representation.

Then §3 to §6 are devoted to detailed study of Feynman diagrams and their contributions to the temporal evolution of the density matrix. Each of diagrams in our treatment is always composed of two usual Feynman diagrams due to the intervention of the density matrix element (§3). This necessitates a slight modification of the usual formulation such as in calculating the ground state energy for a fermion system^{6,7)} (§4 and §6). To obtain the usual master equation, we have to introduce a notion of complementary diagrams which are intimately related to Pauli's exclusion principle and successive collision processes (§5).

In §7, we show that the transition probability becomes asymptotically independent of time for sufficiently long time after the initial setting of the ensemble, if the quantities of the order of the reciprocal of the volume are neglected as in Van Hove's theory.^{1,8)} The time independent transition probability ensures the validity of the usual master equation.

Although the time necessary for the master equation to get valid should be much larger than the effective collision time, it is usually much shorter than the Poincaré cycle. Another restriction is that the initial distribution in the momentum space should be a slowly varying function of unperturbed energy.

In the last section, two limiting cases are treated. For weak coupling limit, we get the same result as Van Hove⁸⁾ obtained, and for low density limit, our result agrees with Prigogine and Résibois' one⁹⁾ and corresponds to the quantum mechanical version of R. Brout's work.¹⁰⁾

§ 2. Hamiltonian and Basic Representation

Let us consider a system of mutually interacting N fermions, of which the hamiltonian is given in the second quantized form:

$$H = H_0 + \lambda V \quad (2.1)$$

$$H_0 = \sum_K \epsilon_K a_K^+ a_K \quad (2.2)$$

$$\epsilon_K = \hbar^2 K^2 / 2m \quad (2.3)$$

$$V = 1/2\Omega \sum_{\substack{K_1, K_2 \\ K_1', K_2'}} v(K_1' - K_1) \delta_{K_1' + K_2' - K_1 - K_2},$$

where m is the mass of a particle, Ω the volume of the system, $\delta_{K_1' + K_2' - K_1 - K_2}$ three products of Kronecker's deltas and a_K^+ , a_K , respectively, are creation and annihilation operators of a fermion with momentum $\hbar K$, which satisfy the commutation relations

$$\begin{aligned} [a_K^+, a_{K'}]_+ &\equiv a_K^+ a_{K'} + a_K a_{K'}^+ = \delta_{K, K'} \\ [a_K^+, a_{K'}^+]_+ &= [a_K, a_{K'}] = 0 \end{aligned} \quad (2.4)$$

and $v(K)$ is the Fourier component of the two-body potential $v(r)$ divided by the coupling parameter λ :

$$\lambda v(K) = \int dr v(r) e^{iK \cdot r}. \quad (2.5)$$

We have assumed here that the perturbation is the sum of interactions due to the two-body potential $v(r)$ which depends only on the inter-particle distance.

We shall consider the statistical ensemble of the systems which is described by the statistical operator $\rho(t)$. The temporal variation of the statistical operator in the interaction representation obeys the Von Neumann equation given by

$$\begin{aligned} \frac{\partial}{\partial t} \rho(t) &= \frac{\lambda}{i\hbar} \{ V(t) \rho(t) - \rho(t) V(t) \} \\ &= \frac{\lambda}{i\hbar} [V(t), \rho(t)] \end{aligned} \quad (2.6)$$

where

$$V(t) = \exp[iH_0 t/\hbar] V \exp[-iH_0 t/\hbar] \quad (2.7)$$

If the perturbation V is given by (2.3), we have

$$\begin{aligned} V(t) &= \frac{1}{2\Omega} \sum_{\substack{K_1, K_2, K_3, K_4}} v(K_1' - K_1) \delta_{K_1' + K_2 - K_1 - K_2'} \\ &\quad \times a_{K_1}^+(t) a_{K_2}^+(t) a_{K_1'}(t) a_{K_2'}(t) \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} a_K(t) &= \exp[iH_0 t/\hbar] a_K \exp[-iH_0 t/\hbar] \\ &= a_K \exp[-i\epsilon_K t/\hbar], \end{aligned} \quad (2.9)$$

$$\begin{aligned} a_K^+(t) &= \exp[iH_0 t/\hbar] a_K^+ \exp[-iH_0 t/\hbar] \\ &= a_K^+ \exp[i\epsilon_K t/\hbar]. \end{aligned} \quad (2.10)$$

The solution of the von Neumann equation in the interaction representation, (2.6), is given in the form

$$\rho(t) = U(t) \rho(0) U^+(t) \quad (2.11)$$

where the unitary operators, $U(t)$ and $U^+(t)$, are expanded in the ordered exponential:

$$\begin{aligned} U(t) &= \sum_{p=0}^{\infty} \left(-\frac{i\lambda}{\hbar} \right)^p \int_{t > t_p > t_{p-1} > \dots > t_1 > 0} dt_p \dots dt_1 \\ &\quad \times V(t_p) V(t_{p-1}) \dots V(t_1), \end{aligned} \quad (2.12)$$

$$\begin{aligned} U^+(t) &= \sum_{q=0}^{\infty} \left(\frac{i\lambda}{\hbar} \right)^q \int_{t > t'_q > t'_{q-1} > \dots > t'_1 > 0} dt'_q \dots dt'_1 \\ &\quad \times V(t'_1) V(t'_2) \dots V(t'_q). \end{aligned} \quad (2.13)$$

The density operator $\rho(t)$ at any instant is uniquely determined by (2.11), provided that the initial condition is properly given. However, the initial setting of the density operator cannot be determined uniquely, since the correlation between phase factors of wave functions of the constituent members of the ensemble cannot be determined directly by our knowledge of the system.

In this article we adopt the postulate of random a priori phases as conventionally introduced in the statistical theory of many-particle system,⁴⁾ though this postulate is not justified and especially in compatible with the spatial inhomogeneity of the system.⁵⁾

The postulate of random phase in the n -representation is expressed as

$$\langle n' | \rho(0) | n \rangle = \langle n | \rho(0) | n \rangle \delta_{K, K'} [n - n'] \quad (2.14)$$

where n stands for a set of occupation numbers $n_K, n_{K'}, \dots$.

§ 3. Diagrams and Wick's Theorem

Let us write the diagonal element of (2-11) in the n -representation

$$\begin{aligned} \langle n | \rho(t) | n \rangle &= \langle n | U(t) \rho(o) U^+(t) | n \rangle \\ &= \sum_{n'} \sum_{n''} \langle n | U(t) | n' \rangle \langle n' | \rho(o) | n'' \rangle \langle n'' | U^+(t) | n \rangle. \end{aligned} \quad (3.1)$$

It is seen from (2.12) and (2.13) that the r.h.s. of the above equation is expressed in terms of the matrix elements such as $\langle n | \alpha_K(t) \beta_K(t) | n' \rangle$ where α and β represent either a creation or an annihilation operator. It is convenient to classify the contribution of these terms with use of Feynman diagrams.

It is necessary to use Wick's theorem³⁾ for the purpose of calculating the diagonal element by a method similar to those employed in other many-body problems. Then, we can proceed in quite analogous way to the case of the calculation of the ground state energy of a many-fermion system based on the time-dependent perturbation theory.⁶⁾⁷⁾ However, there is a difference arising from the fact that we deal with an n - n matrix element referred to the arbitrary set of the occupation numbers, while in the usual perturbation theory the only matrix element referred to the lowest eigenstate n_0 of the unperturbed hamiltonian is concerned, where n_0 corresponds to the set such that the one-particle states inside the Fermi sphere are all occupied and those outside it vacant. Then we shall write Wick's theorem for our system in defining the contraction of operators in a slightly different way. Another different point is that the momentum representation is used instead of the coordinate representation, since it is more convenient for our case.

Taking account of the above points, we shall introduce the following definitions. We define the contraction of two operators α_K and $\beta_{K'}$ with respect to the state n by

$$\dot{\alpha}_K(t) \dot{\beta}_{K'}(t) = \langle n | \alpha_K(t) \beta_{K'}(t) | n \rangle.$$

Then it is evident from the definition that

$$\begin{aligned} \dot{\alpha}_K(t) \dot{\alpha}_{K'}(t) &= \dot{\alpha}_{K^+}(t) \dot{\alpha}_{K'^+}(t) = 0 \\ \dot{\alpha}_{K^+}(t) \dot{\alpha}_{K'}(t') &= \delta_{K^+K'} [K - K'] \exp[i \epsilon_K(t - t')/\hbar] n_K \\ &\equiv -f_K(t - t') \\ \dot{\alpha}_K(t) \dot{\alpha}_{K'^+}(t') &= \delta_{K^+K'} [K - K'] \exp[-i \epsilon_K(t - t')/\hbar] (1 - n_K) \equiv g_K(t - t'). \end{aligned} \quad (3.2)$$

The system of contractions is defined, similarly, for example, by

$$:\dot{\alpha}\dot{\beta}\cdots\dot{\gamma}\cdots\dot{\lambda}\cdots\dot{\mu}\cdots\dot{\nu}: \equiv (-1)^P (\dot{\alpha}\dot{\mu})(\dot{\beta}\dot{\lambda})\cdots(\dot{\gamma}\dot{\nu}), \quad (3.3)$$

where $(-1)^P$ assumes 1 or -1 according as the permutation between the l.h.s. and the

r.h.s. is even or odd.

With use of the above definitions, we find the theorem:

Theorem

$$\begin{aligned} \langle n | \alpha\beta\cdots\gamma | n \rangle &= [\alpha\dot{\beta}\cdots\dot{\gamma} : + \cdots + \alpha\dot{\beta}\cdots\dot{\gamma} : \\ &+ \cdots + \dot{\alpha}\dot{\beta}\cdots\dot{\gamma} : + \cdots + \dot{\alpha}\dot{\beta}\cdots\dot{\gamma} : + \cdots], \end{aligned} \quad (3.4)$$

where the summation in the r.h.s. extends over all the possible combinations of contractions. This is the Wick's theorem for our case and its proof will be given in the Appendix.

Let us consider the case where the density matrix is initially diagonal as given by (2.14). Then we obtain, from (3.1),

$$\begin{aligned} \langle n | \rho(t) | n \rangle &= \sum_{n'} \langle n | U(t) | n' \rangle \langle n' | \rho(o) | n' \rangle \\ &\times \langle n' | U^+(t) | n \rangle. \end{aligned} \quad (3.5)$$

The r.h.s. of the above equation is the same with (3.4) except that the diagonal matrix $\langle n' | \rho(o) | n' \rangle$ is inserted. The insertion of this matrix, however, does not make any difference on the above-mentioned theorem. It gives only a factor $\langle n' | \rho(o) | n' \rangle$ for a definition diagram. Then it is possible to make one-to-one correspondence between the term contributing to $\langle n | \rho(t) | n \rangle$ and the Feynman diagram composed of closed loops of particle lines, which hereafter we refer to vacuum diagram. However, this Feynman diagram consists of two parts. In one part the vertices are arranged to the right with increasing time starting from the middle and in the other part they are arranged to the left (see Fig. 2, 3, etc.). They are connected each other on the vertical line at the middle of the diagram, which will be called the $\rho(o)$ -line. The line drawn at the middle corresponds to the location where $\rho(o)$ is inserted, the left portion corresponding to $U(t)$ and the right one to $U^+(t)$.

It seems useful to give here the prescriptions for writing down the contribution to $\langle n | \rho(t) | n \rangle$ of a given diagram, although they are not so different from the usual ones.¹¹⁾

(1) Each of contractions is expressed by a solid line, which will be called particle line, as illustrated in Fig. 1, where $t^{(1)}$ and $t^{(2)}$ may refer either to the left portion or to the right one of the $\rho(o)$ -line.

(2) Each interaction corresponding to a matrix element of $\partial i \lambda V / \hbar$ is expressed by a

vertical dotted line connecting two vertices, which will be called interaction line, θ being 1 or -1 according as the vertices are located on the right portion or on the left portion.

As an example, let us consider one of the simplest terms second order in λ :

$$\frac{1}{2}\left(-\frac{i\lambda}{\hbar}\right)\left(\frac{i\lambda}{\hbar}\right)\left(\frac{1}{2\Omega}\right)^2\sum_{K_1K_2K_3K_4}\int_0^t dt_1\int_0^{t_1} dt_1'$$
$$\times |v(K_2-K_1)|^2\delta_{K_1}[K_1+K_3-K_2-K_4]$$
$$\times g_{K_1}(t_1-t_1')f_{K_2}(t_1-t_1')g_{K_3}(t_1-t_1')f_{K_4}(t_1-t_1')$$
$$\times \langle \cdots n_{K_1}+1, n_{K_2}-1, n_{K_3}+1, n_{K_4}-1, \cdots \rangle$$
$$\cdots |\rho(o)| \cdots n_{K_1}+1, n_{K_2}-1, n_{K_3}+1, n_{K_4}-1, \cdots \rangle$$

(3.6)

It is obvious that this corresponds to the diagram given by Fig. 2.

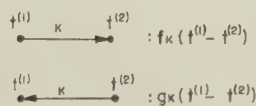


Fig. 1.

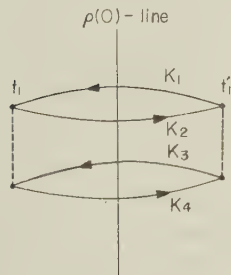


Fig. 2.

We shall consider the general prescriptions for constructing the term corresponding to a given diagram Γ . We can easily find the product of f 's and g 's corresponding to the diagram by the prescriptions (1) and (2). In the first place we have to multiply the product by the diagonal element of the initial density matrix $\langle n'|\rho(o)|n\rangle$. Since the difference between two sets n and n' appears only in connection with the wave numbers $K_1, K_2, \cdots$ (from right) and $K_1', K_2', \cdots$ (from left) of particle lines which cross the $\rho(o)$ -line, the set n' is $n_{K_1}, \cdots, n_{K_1}+1, n_{K_2}+1, \cdots, n_{K_2'}-1, n_{K_3'}-1, \cdots$ and we obtain

(3) Multiply the product by

$$\langle \cdots, n_{K_1}+1, n_{K_2}+1, \cdots, n_{K_1'}-1, n_{K_2'}-1, \cdots$$
$$|\rho(o)| \cdots, n_{K_1}+1, n_{K_2}+1, \cdots, n_{K_1'}-1,$$
$$n_{K_2'}-1, \cdots \rangle$$

corresponding to the particle lines crossing the $\rho(o)$ -line from left or right.

Then we have the further three prescriptions

to complete the contribution of a given diagram to the r.h.s. of (3.5).

(4) Integrate with respect to the time variables over the ranges

$$t>t_p>\cdots>t_1>0; \quad t>t_q>\cdots>t_1'>0$$

where p and q are the number of interaction lines in the left portion and in the right portion of the $\rho(o)$ -line respectively.

(5) Take the summation over all the wave numbers which correspond to the particle lines in the given diagram.

(6) Divide the integral by $(-1)^h g(\Gamma)$ where h is the number of closed loops of particle lines and $g(\Gamma)$ is the number of permutations (including identity) which bring the given diagram Γ into the diagrams topologically equivalent to itself.

The necessity of the symmetry number is rather obvious for the case of the simplest diagram given in Fig. 2. Since the summation over the intermediate states extends over all the possible values of wave numbers, each arrangement of vertices and lines is counted twice in the summation and consequently we have to divide the integral by two corresponding to $g(\Gamma)=2$.

In the foregoing treatment we have restricted ourselves to the diagonal elements. However, it is possible to extend our method in the present and the next sections to the case of the off-diagonal elements, as will be seen in the Appendix.

§ 4. Application of Linked Cluster Expansion

Having established the one-to-one correspondence between a Feynman diagram and a term in the right hand side of (3.5), we may decompose the temporal evolution of the density matrix into the contribution of various diagrams

$$\sum_{\Gamma} \sum_{n'} \sigma_{\Gamma}^{(n)}(n|n';t) \langle n'|\rho(o)|n\rangle$$

(4.1)

where the first summation extends over all the vacuum diagrams. The superscript (n) represents the reference state to which the definition of contraction is referred. For example, $\sigma_{\Gamma}^{(n)}(n|n';t)$ for the diagram given in Fig. 2, Γ_1 , is

$$\sigma_{\Gamma_1}^{(n)}(n|n';t) = \sigma_{\Gamma_1}^{(n)}(\cdots, n_{K_1}, n_{K_2}, n_{K_3}, n_{K_4}, \cdots |$$
$$\cdots, n_{K_1}+1, n_{K_2}-1, n_{K_3}+1, n_{K_4}-1, \cdots; t)$$
$$\text{for } K_1+K_3-K_2-K_4=0,$$
$$=0 \quad \text{otherwise.}$$

We shall note here that if we fix the reference state n , we can generally construct the contribution $\sigma_{\Gamma}^{(n)}(n''|n';t)$ for a given diagram according to the prescriptions given in the preceding section, the final state not being necessarily identical with the reference state n . Then we may regard $\sigma_{\Gamma}^{(n)}(n''|n';t)$ as the $n''-n'$ matrix element of a matrix $\sigma_{\Gamma}^{(n)}(t)$.

On the other hand, so far as we concern the diagonal elements of the density matrix, we may regard $\langle n|\rho|n \rangle$ as the component of the vector referred to the axis n . Then (4.1) implies that $\sigma_{\Gamma}^{(n)}(t)$ is an operator acting on the vector of which components are $\langle n|\rho|n \rangle$'s and is rewritten symbolically as

$$\begin{aligned} \sum_{\Gamma} \sum_{n'} \sigma_{\Gamma}^{(n)}(n''|n';t) \langle n'|\rho(o)|n' \rangle \\ = \langle n''|\sigma_{\Gamma}^{(n)}(t)\rho(o)|n' \rangle \end{aligned} \quad (4.2)$$

Thus we can make each Feynman diagram Γ correspond to a $\sigma_{\Gamma}^{(n)}$ -operator.

Let us now consider some properties of the $\sigma_{\Gamma}^{(n)}$ -operators. First, sum of two $\sigma_{\Gamma}^{(n)}$ -operators is clearly corresponds to the sum of contributions of two diagrams. According to the general rule for matrix multiplication, we may also define the product of $\sigma_{\Gamma}^{(n)}$ -operators by

$$\begin{aligned} \langle n'''|\sigma_{\Gamma}^{(n)}(t)\sigma_{\Gamma'}^{(n)}(t)|n'' \rangle = \sum_{n'''} \sum_{n''} \sigma_{\Gamma}^{(n)}(n'''|n'';t) \\ \sigma_{\Gamma'}^{(n)}(n''|n';t) \langle n'|\rho(o)|n' \rangle \end{aligned} \quad (4.3)$$

Since the matrix element of $V(t)$ depends only on the transferred momentum and energy*, it is determined by the set of the differences of the occupation numbers for the final and initial states, $n_1''-n_1'$, $n_2''-n_2'$, $\dots$, which will be denoted by $n''-n'$. Hence $\sigma_{\Gamma}^{(n)}(n''|n';t)$ depends only on the set of the differences $n''-n'$:

$$\sigma_{\Gamma}^{(n)}(n''|n';t) = \sigma_{\Gamma}^{(n)}(n''-n';t) \quad (4.4)$$

$$n''-n' \equiv (\dots, n_{K1}''-n_{K1}', n_{K2}''-n_{K2}', \dots) \quad (4.5)$$

From (4.3) and (4.5), it can be shown that

$$\sigma_{\Gamma}^{(n)}(t) \sigma_{\Gamma'}^{(n)}(t) = \sigma_{\Gamma\Gamma'}^{(n)}(t) \sigma_{\Gamma}^{(n)}(t) \quad (4.6)$$

It is in general known that the matrix element of $\sigma_{\Gamma}^{(n)}(t)$ may involve the terms which diverge more strongly than N as $N \rightarrow \infty$ and do more strongly than t as $t \rightarrow \infty$.* To avoid this divergence difficulty, it is necessary to rearrange the terms in such a way that it

may be proportional to N and t as $N \rightarrow \infty$, $t \rightarrow \infty$. This will be achieved to a certain extent by rearrangement with use of the linked cluster expansion, which will be described in the remaining of this section.

We shall classify the diagram into linked and unlinked diagrams. If any two of vertices of a diagram are connected directly or indirectly by at least one particle or interaction line, it is called a linked diagram, and otherwise it is called an unlinked diagram. The diagrams in Fig. 3 and 5 (a)–(f) are unlinked, whereas those in Fig. 2 and 5 (g)–(i) are linked. The diagram without vertex, of which the contribution is mere multiplication of 1, is

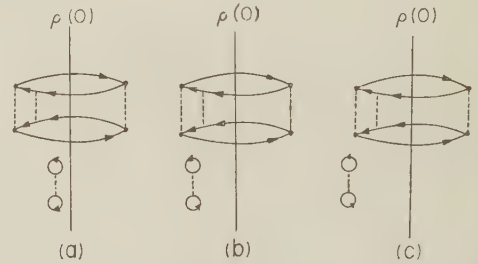


Fig. 3. A simple example of diagrams belong to the same family.

conventionally treated as an unlinked diagram. Thus we may say that an unlinked diagram except the simplest one without vertex is always composed of two or more linked diagrams.

Let us denote the constituent linked-diagrams of a given diagram Γ by $\Gamma_1, \Gamma_2, \dots$. Then we may write

$$\Gamma = n_1 \Gamma_1 + n_2 \Gamma_2 + \dots \quad (4.7)$$

where $n_1, n_2, \dots$ are the numbers of the linked diagrams $\Gamma_1, \Gamma_2, \dots$, respectively. However, there exist, in general, a certain number of diagrams which are composed of the same set of linked part, and consequently the expression (4.7) does not correspond uniquely to a definite diagram. We shall call a set of diagrams composed of the same linked parts a family of diagrams and will be denoted by $[I]$. These diagrams given in Fig. 3 form a family of diagrams.*

It is evident that the summation over the wave numbers can be carried out for the constituent linked parts independently each other, and these diagrams are connected with each

* It is generally true when there is no external field.

* For the physical implication of $t \rightarrow \infty$, see §7.

other only through the restriction on the integration with respect to time variables. It is, however, possible to remove the above restriction on the time variables by collecting the contributions of the diagrams belonging to the same family $[\Gamma]$. Then integration for every linked part is performed from 0 to t irrespective of the other linked parts, and integrations for all the linked parts yield

$$\sigma_{\Gamma}^{(n)}(t) = \frac{1}{n_1! n_2! \dots} [\sigma_{\Gamma_1}^{(n)}(t)]^{n_1} [\sigma_{\Gamma_2}^{(n)}(t)]^{n_2} \dots \quad (4.8)$$

where the $\sigma_{\Gamma}^{(n)}$ -operators are all commutative each other according to (4.6). From combination analysis we have obtained the numerical factor

$$\frac{1}{n_1! n_2! \dots} = [g(\Gamma_1)]^{n_1} [g(\Gamma_2)]^{n_2} \dots / g(\Gamma) n_1! n_2! \dots$$

Since the family of diagrams are uniquely determined by the set of numbers $(n_1, n_2, \dots)$, the sum over all the families of diagrams is the same as the sum over the set of numbers $(n_1, n_2, \dots)$ and hence we obtain

$$\sum_{[\Gamma]} \frac{1}{n_1! n_2! \dots} [\sigma_{\Gamma_1}^{(n)}(t)]^{n_1} [\sigma_{\Gamma_2}^{(n)}(t)]^{n_2} \dots = \exp [\sigma_L^{(n)}(t)], \quad (4.9)$$

which is equivalent to

$$\langle n | \rho(t) | n \rangle = \langle n | \exp [\sigma_L^{(n)}] \rho(o) | n \rangle, \quad (4.10)$$

where

$$\sigma_L^{(n)}(t) = \sum_{\Gamma \text{ linked}} \sigma_{\Gamma}^{(n)}(t). \quad (4.11)$$

The above result is the one called linked cluster expansion and is different from usual ones only in existence of the $\rho(o)$ -line.

It should be noted here that Eq. (4.11) has been derived without making any approximation, and hence it is merely an alternative expression for the solution of the von Neumann equation (2.6), which is much more convenient in dealing with the dissipative feature of the system.

Furthermore, as will be seen in Appendix, the contribution of any linked diagram is proportional to N as $N \rightarrow \infty$, so that the divergence difficulty from the higher power terms

* As is illustrated in Fig. 3, the diagrams belonging to the same family are drawn by the rearrangements of vertices in either side of the $\rho(o)$ -line in such a way as any order of vertices within each linked diagram should be kept unchanged. It must be noted that this rearrangement should not be made between the vertices which belong to the different portions of the $\rho(o)$ -line.

in N does not appear. In this respect, our method seems to be more satisfactory than Van Hove's one,¹⁾ in which the solution is expanded in terms of the irreducible diagonal parts, since each irreducible diagonal part of Van Hove may contain such terms as divergent more rapidly than N , as illustrated in Fig. 4. (Hugenholtz's diagrams¹²⁾ are used).

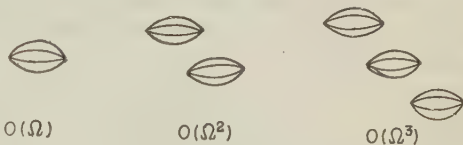


Fig. 4. Irreducible diagonal parts which diverge in higher powers of Ω .

§ 5. Complementary Diagrams

At first sight, the differentiation of (4.10) with respect to time seems to lead us directly to the usual master equation. However, derivation of the master equation from (4.10) is not really so simple. This is possible only for sufficiently large t , as will be seen below. Differentiating (4.10) with respect to t , we obtain

$$\frac{d}{dt} \langle n | \rho(t) | n \rangle = \sum_{n'} \left\{ \frac{d}{dt} \sigma_L^{(n)}(n-n'; t) \right\} \times \langle n' | \exp [\sigma_L^{(n)}(t)] \rho(o) | n' \rangle \quad (5.1)$$

The first point we have to keep in mind is that the contribution of the linked diagrams may diverge more rapidly than t as $t \rightarrow \infty$, and hence does not give proper transition probability. The second point is that $\langle n' | \exp [\sigma_L^{(n)}(t)] \rho(o) | n' \rangle$ is not equal to $\langle n' | \rho(t) | n' \rangle$ since the reference states for σ_L -operators are not the same. In other words, (5.1) is not necessarily identical with

$$\frac{d}{dt} \langle n | \rho(t) | n \rangle = \sum_{n'} \left\{ \frac{d}{dt} \sigma_L^{(n)}(n-n'; t) \right\} \times \langle n' | \exp [\sigma_L^{(n)}(t)] \rho(o) | n' \rangle \quad (5.2)$$

from which we expect to derive the master equation.

Let us now consider the second point above-mentioned more in detail. We shall consider, for simplicity, the following term in (5.1)

$$\sum_{n''} \sum_{n'} \left\{ \frac{d}{dt} \sigma_{\Gamma_1}^{(n)}(n-n'; t) \right\} \sigma_{\Gamma_2}^{(n)}(n'-n''; t) \times \langle n'' | \rho(o) | n'' \rangle \quad (5.3)$$

where Γ_1 and Γ_2 are both linked diagrams crossing the $\rho(o)$ -line and second order in λ (see Fig. 5). The corresponding terms in (5.2) is

$$\sum_{n'} \sum_{n''} \left\{ \frac{d}{dt} \sigma_{\Gamma_1}^{(n)}(n-n'; t) \right\} \sigma_{\Gamma_2}^{(n')}(n'-n''; t) \times \langle n'' | \rho(o) | n' \rangle \quad (5.4)$$

According to the definition of contraction, the difference between (5.3) and (5.4) appears only when Γ_2 involves such a particle line K that it gives different values for n_K and n'_K . As seen from Fig. 5 (a) and (b), it takes place only when one of the particle lines of Γ_1 which cross the $\rho(o)$ -line has the wave number K .

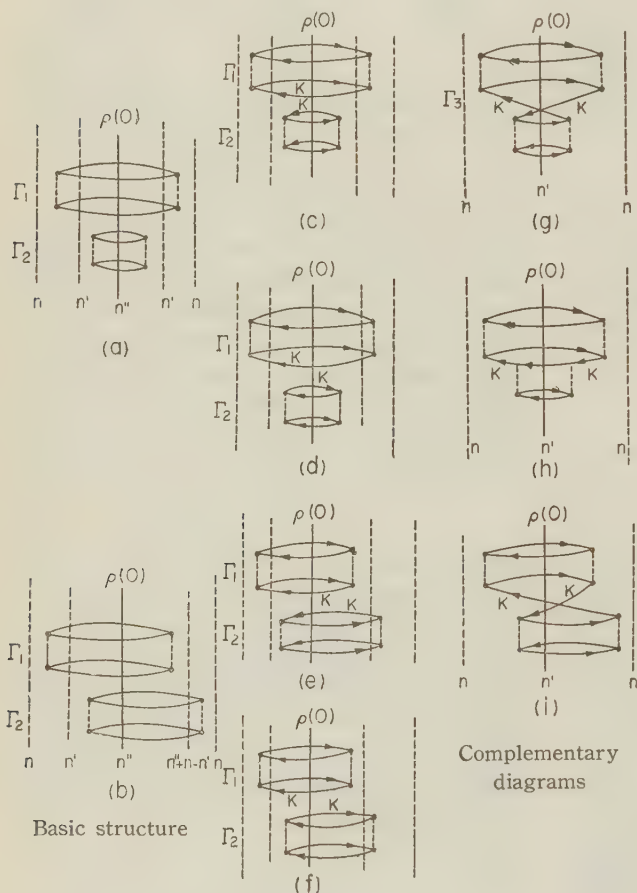
diagrams of Fig. 5 (c), (d), to which we refer as *a*-type diagrams, as will be demonstrated in §7. Then the contribution of the *b*-type diagrams may be neglected and we have only to consider the *a*-type diagrams, so far as the long time behaviour is concerned. This is also the case for more complicated diagrams, if we call *a*-type or *b*-type according as the whole Γ_2 is confined between the two interaction lines of Γ_1 nearest to the $\rho(o)$ -line on both sides, or not.

Returning to the simplest diagrams of Fig. 5, we first consider the case as given by Fig. 5(c). Then its contribution to (5.4) vanishes since it involves the factor $n_K n'_K = n_K(1-n_K) = 0$, while its contribution to (5.3) does not vanish. However, it should be noted here that there exists the diagram given by Fig. 5 (g)*, which yields the contribution of the equal magnitude and opposite sign to that of (c). This diagram is produced from (c) by interchanging the final vertices with the two particle lines of the wave number K . We shall refer to (g) as the complementary diagram to (c). Then the contribution lost in changing the reference state from (n) to (n') for the diagram Γ_2 of Fig. 5 (c) is in the equation (5.3) just cancelled with the contribution of its complementary diagram Fig. 5 (g). In general, the existence of such complementary diagrams to more complicated diagrams of this type may be rather comprehensive if we remind that this is a direct consequence of Pauli's exclusion principle.

We shall next consider the case of Fig. 5 (d). Contrary to the former case, the contribution to (5.3) vanishes because it involves the factor $n_K(1-n_K)$, while the contribution to (5.4) does not vanish. However, it is easily seen that the diagram Fig. 5 (d) makes the same contribution to (5.4) with that of Fig. 5 (h). In this case, we refer to

* If we denote by Γ_3 the complementary diagram given by (g), then we obtain, corresponding to (5.3)

$$\sum_{n'} \left\{ \frac{d}{dt} \sigma_{\Gamma_3}^{(n)}(n-n'; t) \right\} \langle n' | \rho(o) | n' \rangle \quad (5.5)$$



Concerning diagrams
Fig. 5.

Therefore, it is seen that the difference between (5.3) and (5.4) arises from the parts shown in Fig. 5 (c), (d), (e) and (f). Out of the four diagrams, those given by (c) and (e) have the particle line with the same wave number K which are in the same direction, whereas those given by (d) and (f) have those in the opposite directions. However, for sufficiently long time, the contribution of diagram of Fig. 5 (e), (f), to which we refer as *b*-type diagrams, is small by the factor $1/t$ compared to that of

the diagram Fig. 5 (h) as the complementary diagram to that of Fig. 5 (d). Then the contribution gained in changing the reference state from (n) to (n') for the diagram Γ_2 of Fig. 5 (d) is just equal to that of the complementary diagram Fig. 5 (h). This is also the case for more complicated diagrams of the same kind.

These results are generalized to the products of more than two $\sigma_{L^{(n)}}(t)$ s. Then we can change the reference state $\sigma_{L^{(n)}}(t)$ of Eq. (5.1) to (n') . Since the contribution of complementary diagrams is not affected by the change of the reference state, we get

$$\begin{aligned} \frac{d}{dt} \langle n | \rho(t) | n \rangle &= \sum_{n'} \frac{d}{dt} \{ \sigma_{L^{(n)}}(n-n'; t) \\ &\quad - \sigma_{L^{(n)}}(n-n'; t) \} \langle n' | \exp [\sigma_{L^{(n)}}(t)] \rho(o) | n' \rangle \\ &= \sum_{n'} \left\{ \frac{d}{dt} \sigma_{L^{(n)}}(n-n'; t) \right\} \langle n' | \rho(t) | n' \rangle \end{aligned} \quad (5.6)$$

where $\sigma_{L^{(n)}}(n-n'; t)$ is the total contribution of the complementary diagrams and $\sigma_{L^{(n)}}(n-n'; t)$ the total contributions of all the linked diagrams except the complementary ones. The contributions of $O(1/t)$ are neglected in the above.

From the unitarity of $U(t)$ we have

$$\langle n | U(t) U^\dagger(t) | n \rangle = 1 \quad (5.7)$$

and consequently

$$\frac{d}{dt} \langle n | U(t) U^\dagger(t) | n \rangle = 0, \quad (5.8)$$

and

$$\sum_{n' \neq n} \frac{d}{dt} \sigma_{L^{(n)}}(n-n'; t) = - \frac{d}{dt} \sigma_{L^{(n)}}(o; t). \quad (5.9)$$

Then we can rewrite (5.6) as

$$\begin{aligned} \frac{d}{dt} \langle n | \rho(t) | n \rangle &= \sum_{n' \neq n} \frac{d}{dt} \sigma_{L^{(n)}}(n-n'; t) \\ &\quad \times \{ \langle n' | \rho(t) | n' \rangle - \langle n | \rho(t) | n \rangle \}. \end{aligned} \quad (5.10)$$

If the transition rate $\frac{d}{dt} \sigma_{L^{(n)}}(n-n'; t)$ is positive definite and independent of time, (5.10) becomes identical with the usual master equation. We shall discuss about this condition in § 7.

Before concluding this section, we shall mention of some remarks on the complementary diagrams.

First, although we have defined the complementary diagrams only for the a -type dia-

grams, we can easily find that the diagram Fig. 5 (i) is in a similar complementary relation to the b -type diagram Fig. 5 (e). But some of b -type diagrams, such as that of Fig. 5 (h), have no complementary diagrams in a similar sense, so that the neglect of $O(1/t)$ is essential in derivation of Eq. (5.6).

In general, the complementary diagram is always linked and has two particle lines of the same direction and with the same wave number as a direct consequence of the conservation of momentum. This is easily shown in the following manner. The complementary diagram cancels the contributions of such diagrams as Fig. 5 (c), (d), (e). However, the contribution of these diagrams are the part of $O(1/t)$ of the contribution of diagrams Fig. 5 (a), (b). If these contributions cancel with those of their complementary diagrams, the restriction other than the momentum conservation should not be imposed on the wave numbers of particle lines of the complementary diagrams, since each complementary diagram is composed of one linked diagram while the diagram of Fig. 5 (a) or (b) is composed of two.

But the diagrams having two particle lines with the same wave numbers directly due to the momentum conservation are not necessarily the complementary diagrams. This will be seen from the diagram shown in Fig. 11 (a). This diagram is not complementary diagram. In general, if the two particle lines with the same wave number K are confined to the same side of the $\rho(o)$ -line, they are not complementary diagrams. This is because, in the diagram contributing to the transition rate (Γ_1 in Fig. 5), the particle line with the wave number K under consideration should cross the $\rho(o)$ -line. We shall consider such diagrams in the next section.

Secondly, the complementary diagram, as given by Fig. 5 (h), corresponds to the successive collision in classical language, and it causes the higher order divergence in t for $\sigma_{L^{(n)}}(n-n'; t)$. Hence the exclusion of such complementary diagrams removes some of the terms which are divergent in the limit of infinite t from the transition probability rate. But there remain other terms which diverge in the limit $t \rightarrow \infty$ and we shall deal with them in the next section. There further remain the diagrams among those correspond-

ing to successive collisions just as will be seen from the example of Fig. 5 (f). Such successive collisions corresponding to such diagrams are nothing but those reducible to higher order multiple collision because they follow so closely each other. It is obvious that these terms give the contribution of $O(1/t)$ compared with the ordinary successive collisions.

On the other hand, complementary diagrams as Fig. 5 (g), (i) are obtainable only with neglect of Pauli's exclusion principle. It is rather natural consequence that they give no contribution to the transition probability.

Finally we should note that the terms of $O(1/\mathcal{Q})$ have been ignored in (5.6). Since, for example, there does not exist the complementary diagram which cancels the contribution of the diagram as shown in Fig. 6, because two independent restrictions are imposed on two sets of particle lines in this diagram, its contribution is $O(1/\mathcal{Q})$. However, it should be added that the cancellation due to Pauli's principle are exactly fulfilled.

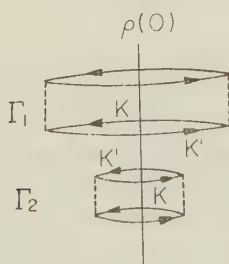


Fig. 6.

§ 6. Renormalization and Reduction of Diagrams

To complete the removal of the divergent terms at $t \rightarrow \infty$ from the transition probability rate, we perform the renormalization of particle lines in an analogous way to the theory of one-body Green functions. However, in our case, the renormalization should be made only for the particle lines which are confined to one side of the $\rho(o)$ -line.

Let us confine our discussions, for the time being, only to the left portion of the $\rho(o)$ -line. A free particle line which connects two vertices corresponds to the contribution of f_K or g_K . Similarly let us designate by F_K or G_K the contribution of a renormalized particle line, which is expressed by a heavy line in

Fig. 8 or Fig. 9. It corresponds to the total contribution of all the particle lines which end with the same wave number K at the two terminal vertices, between which there may, or may not, be any diagram which attaches itself only to the concerning particle line. The attached diagram may be decomposed in such a way as shown in Fig. 9. We call



Fig. 7. Examples of renormalizable particle lines.

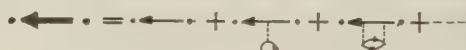
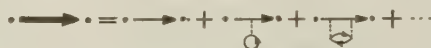


Fig. 8. Renormalized particle line.

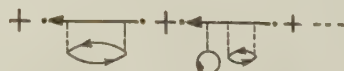
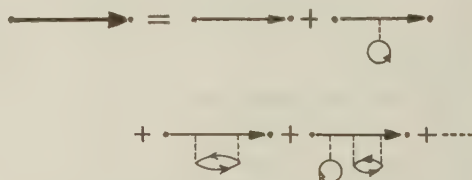


Fig. 8. Renormalized particle line.

an attached part which cannot be decomposed into two parts an irreducible self-energy part, representing it as a whole by a square as in Fig. 9 and designating its whole contribution by $\Sigma(K, t)$.

Then, as is well known in the theory of Green functions, F_K and G_K satisfy the following integral equations:

$$F_K(t) = f_K(t) + \int_0^t dt_1 \int_0^{t_1} dt_2 f_K(t-t_2) \Sigma(K, t_2-t_1) \times F_K(t_1), \quad (6.1)$$

$$G_K(t) = g_K(t) + \int_0^t dt_1 \int_0^{t_1} dt_2 g_K(t-t_2) \Sigma(K, t_2-t_1) \times G_K(t_1). \quad (6.2)$$

Using the Fourier transform, we get the solutions of (6.1) and (6.2) in the form

$$F_K(t) = \frac{1}{2\pi} \int_C d\eta \frac{i\hbar n_K \exp[i\eta t/\hbar]}{\varepsilon_K - \eta - i\hbar n_K \Sigma(K, \eta)} \quad (6.3)$$

$$G_K(t) = \frac{1}{2\pi} \int_{C'} d\eta \frac{i\hbar(1-n_K) \exp[-i\eta t/\hbar]}{\eta - \varepsilon_K - i\hbar(1-n_K) \Sigma(K, \eta)} \quad (6.4)$$

$t > 0$

where $\Sigma(K, \eta)$ is the Fourier transform of $\Sigma(K, t)$,

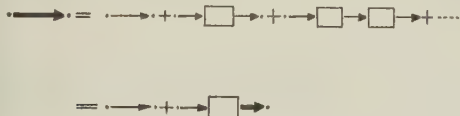


Fig. 9. Expansion of the renormalized particle line in terms of self energy part.

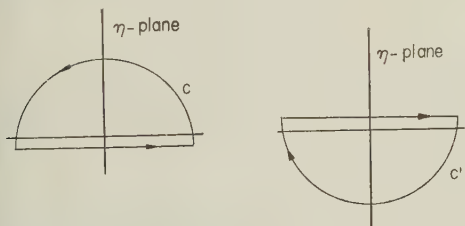


Fig. 10.

and the contours C and C' are such as shown in Fig. 10.

Generally the integrands of (6.3) and (6.4) may have many poles within the contours. In this article, however, we concern for practical interests only cases where only one simple pole exists on the real axis. Then we can write

$$F_K(t) = \rho_K n_K \exp[i\eta_K t/\hbar] \quad (6.6)$$

$$G_K(t) = \rho_K(1-n_K) \exp[-i\eta_K t/\hbar] \quad (6.7)$$

where η_K is the pole of the above integrands and ρ_K is the real coefficient.*

Quite similar results are obtained when we confine our discussions to the right portion of

* Since $\Sigma(K, \eta)$ appears in the integrands only through the expression $n_K \Sigma(K, \eta)$ or $(1-n_K) \Sigma(K, \eta)$, both η_K and ρ_K can be determined independently for the two cases; $n_K=0$ and $(1-n_K)=0$.

the $\rho(o)$ -line, and the only difference is that $t < 0$ for this case.

We now return to the full linked diagram and make the reduction of linked diagrams, which is essential to eliminate the appearance of higher order poles from the integrand of time integrations in $\sigma_r^{(n)}(n-n'; t)$, as we show in the next section.

A linked diagram is called reducible, if it contains at least two particle lines of the same direction and with the same momentum, as a direct consequence of the momentum conservation, and irreducible, if it is not reducible. For example, the complementary diagrams discussed in the preceding section are all reducible. Then any reducible diagram can be reduced to an irreducible diagram uniquely. Further, the total contribution of all the diagrams that can be reduced to the same irreducible diagram I' , but that are not com-

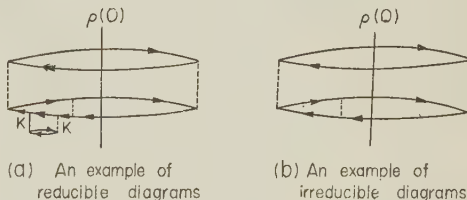


Fig. 11.

plementary diagrams, (including the contributing from I' itself), is just equal to the contribution of the irreducible diagram I' of which every particle line which does not cross the $\rho(o)$ -line is replaced by the heavy line with its momentum, that is to say, for the particle line does not cross the $\rho(o)$ -line, the contribution f_K or g_K is replaced by F_K or G_K . Then to calculate the total contribution of the linked diagrams except the complementary diagrams, we have only to consider the irreducible diagrams of which every particle line confined to one side of the $\rho(o)$ -line is replaced by the corresponding renormalized particle line.

§7. Long Time Behaviour of the System.

In this section, we investigate the asymptotic long time behaviour of the system. By long time, we mean a time, which is sufficiently large compared to the time characteristic to the effective potential and to the time characteristic to the dispersion of initial distribution in momentum space, and which is at the same time far shorter than the time

characteristic to the size of the system, or in other words, the time related to the Poincaré cycle of the system. Thus we introduce three characteristic times, or we may say three characteristic energies. The first one $\delta_v E$ is the typical transferred energy through one effective interaction; the second one $\delta_p E$ is the energy interval in which the initial density matrix remains almost constant and the last one $\delta_i E$ is the typical difference between adjoining energy levels. Then our nomenclature long time is the time which satisfies the inequalities

$$\begin{aligned} \tau_i &\equiv \hbar/\delta_i E \gg t \\ t &\gg \tau_v \equiv \hbar/\delta_v E \\ &\gg \tau_p \equiv \hbar/\delta_p E \end{aligned} \quad (7.1)$$

In the present theory, the existence of such time interval is quite essential. The first condition of the above inequalities is necessary for the energy level of the system to be regarded as continuous and is always satisfied by setting $\Omega \rightarrow \infty$. The second condition $t \gg \tau_v$ is also fulfilled when there exists an effective potential of finite force range. While these first two conditions are purely mechanical, the last one $t \gg \tau_p$ is a statistical one and is not justified at very low temperatures, where an abrupt change of occupation probability in momentum space takes place near the Fermi surface. For the present we assume the existence of such time interval and confine our discussions to this time scale.

Let us return to the collision factor of (5.10). We consider only the contribution of the irreducible linked diagram in which every particle line is replaced by the renormalized line in the sense mentioned in §6. Our present task is to carry out the time integration and investigate its long time asymptotic behaviour, showing that the transition probability rate of Eq. (5.10) becomes independent of t and that this equation reduces to the usual master equation.

The time dependent part of the contribution has a form

$$\begin{aligned} &\left(-\frac{i\lambda}{\hbar}\right)^p \left(\frac{i\lambda}{\hbar}\right)^q \int \cdots \int_{t > t_p > \cdots > t_1 > 0} dt_p \cdots dt_1 \int \cdots \int_{t > t_{q'} > \cdots > t_1' > 0} dt_{q'} \cdots dt_1' \exp[-i\Delta\mathcal{E}_p t_p/\hbar] \cdots \exp[-i\Delta\mathcal{E}_1 t_1/\hbar] \\ &\times \exp[i\Delta\mathcal{E}_1' t_1'/\hbar] \cdots \exp[i\Delta\mathcal{E}_q' t_{q'}/\hbar], \end{aligned} \quad (7.2)$$

where $\Delta\mathcal{E}_j$ and $\Delta\mathcal{E}_j'$ are the renormalized trans-

ferred energies* from left to right at vertices corresponding to the times t_j and t_j' , respectively. Rewriting the time variables

$$\begin{aligned} &t_1 \rightarrow t_1, \quad t_2 - t_1 \rightarrow t_2, \quad \cdots, \quad t_p - t_{p-1} \rightarrow t_p \\ &t_1' \rightarrow t_1', \quad t_2' - t_1' \rightarrow t_2', \quad \cdots, \quad t_q - t_{q-1}' \rightarrow t_q' \\ &\int \cdots \int_{t > t_p > \cdots > t_1 > 0} dt_p \cdots dt_1 \rightarrow \int \cdots \int_{\substack{t_1 > t_2 > 0, \dots, t_p > 0 \\ t_1 + t_2 + \cdots + t_p < t}} dt_p \cdots dt_1 \\ &= \int_0^\infty \cdots \int_0^\infty dt_p \cdots dt_1 \frac{1}{2\pi i} \int_{-\infty + i\beta}^{-\infty + i\beta'} d\mathcal{E} \\ &\times \exp[i\mathcal{E}(t_1 + t_2 + \cdots + t_p - t)/\hbar], \\ &\beta > 0 \end{aligned}$$

and putting

$$\begin{aligned} \Delta\mathcal{E}_p + \Delta\mathcal{E}_{p-1} + \cdots + \Delta\mathcal{E}_j &\equiv \mathcal{E}_j \quad (j=1, 2, \dots, p) \\ -\Delta\mathcal{E}_q' - \Delta\mathcal{E}_{q-1}' - \cdots - \Delta\mathcal{E}_j' &\equiv \mathcal{E}_j' \quad (j=1, 2, \dots, q) \\ \mathcal{E}_1 &= \mathcal{E}_1', ** \end{aligned}$$

we obtain from (7.2)

$$\begin{aligned} &\left(-\frac{1}{4\pi^2}\right) \left(-\frac{i\lambda}{\hbar}\right)^p \left(\frac{i\lambda}{\hbar}\right)^q \int_0^\infty \cdots \int_0^\infty dt_p \cdots dt_1 \\ &\int_0^\infty \cdots \int_0^\infty dt_{q'} \cdots dt_1' \int_{-\infty + i\beta}^{-\infty + i\beta'} \frac{d\mathcal{E}}{\mathcal{E}} \int_{-\infty + i\beta'}^{-\infty + i\beta} \frac{d\mathcal{E}'}{\mathcal{E}'} \exp[-i(\mathcal{E} + \mathcal{E}')t/\hbar] \\ &\times \left\{ \exp[i(\mathcal{E} - \mathcal{E}_p)t_p/\hbar] \cdots \exp[i(\mathcal{E} - \mathcal{E}_1)t_1/\hbar] \right\} \\ &\times \left\{ \exp[i(\mathcal{E}' + \mathcal{E}_1)t_1'/\hbar] \cdots \exp[i(\mathcal{E}' + \mathcal{E}_q')t_{q'}/\hbar] \right\} \\ &\beta > 0, \quad \beta' > 0 \end{aligned} \quad (7.3)$$

As $\beta > 0$, $\beta' > 0$, all the integrals over time variables converge absolutely so that we may interchange the order of time integrations and we get

$$\begin{aligned} &(-1)^{q+1} \frac{1}{4\pi^2} \lambda^{p+q} \int_{-\infty + i\beta}^{-\infty + i\beta'} d\xi \int_{-\infty + i\beta'}^{-\infty + i\beta'} d\eta \exp[-2i\xi t/\hbar] \\ &\frac{1}{\xi + \eta/2} \frac{1}{\xi - \eta/2} \frac{1}{\xi + (\eta/2 - \mathcal{E}_1)} \frac{1}{\xi - (\eta/2 - \mathcal{E}_1)} \\ &\times \frac{1}{\xi + (\eta/2 - \mathcal{E}_p)} \cdots \frac{1}{\xi + (\eta/2 - \mathcal{E}_2)} \frac{1}{\xi - (\eta/2 - \mathcal{E}_2)} \\ &\cdots \frac{1}{\xi - (\eta/2 - \mathcal{E}_q')} \end{aligned} \quad (7.4)$$

$$\beta > |\beta'| \geq 0$$

where we have introduced the new variables

* Strictly speaking, if the particle line crosses the $\rho(0)$ -line, the corresponding energy is not the renormalized energy.

** The energy $\mathcal{E}_j$ corresponds to the energy between t_j and t_{j-1} , when we take the energy at t as the base.

$$\begin{aligned}\frac{\varepsilon + \varepsilon'}{2} &= \xi, & \varepsilon - \varepsilon' &= \eta \\ \varepsilon &= \xi + \eta/2, & \varepsilon' &= \xi - \eta/2\end{aligned}\quad (7.5)$$

Differentiating with respect to t , we get

$$\begin{aligned}(-1)^{q+1} \frac{1}{4\pi^2} \lambda^{p+q} \int_{-\infty+i\beta}^{\infty+i\beta} d\xi \int_{-\infty+i\beta'}^{\infty+i\beta'} d\eta (-2i\xi/\hbar) \\ \times \exp[-2i\xi t/\hbar] \\ \times \frac{1}{\xi + \frac{\eta}{2}} \frac{1}{\xi - \frac{\eta}{2}} \frac{1}{\xi + \left(\frac{\eta}{2} - \varepsilon_1\right)} \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon_1\right)} \\ \times \frac{1}{\xi + \left(\frac{\eta}{2} - \varepsilon_p\right)} \dots \frac{1}{\xi + \left(\frac{\eta}{2} - \varepsilon_3\right)} \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon'_2\right)} \\ \dots \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon'_q\right)}\end{aligned}\quad (7.6)$$

Thus our problem is reduced to the study of poles of the integrand of the above expression. As we show in the following, the important contribution comes from the pair of poles of the form

$$\xi = \pm(\eta - x)$$

They contribute $\delta\left[\frac{x}{\hbar}\right]$, which ensures the conservation of energy. Unpaired poles also contribute, but their contributions cannot be expressed in a simple form and do not ensure the conservation of energy for the intermediate states. However, the results give the usual collision factor of the dissipative master equation, if we assume its positive definiteness.

To see this, we first notice that any two of $0, \varepsilon_1, \varepsilon_2, \dots, \varepsilon_p, \varepsilon'_2, \dots, \varepsilon'_q$, are different each other* so that such a pair of singularities as mentioned above only comes from the parts

$$\frac{1}{\xi + \frac{\eta}{2}} \frac{1}{\xi - \frac{\eta}{2}} \frac{1}{\xi + \left(\frac{\eta}{2} - \varepsilon_1\right)} \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon_1\right)}$$

That the contribution of these parts correspond to that of pseudopoles of Van Hove is rather evident. For simplicity, we only consider the simplest case,

$$-\frac{1}{4\pi^2} \lambda^3 \int_{-\infty+i\beta}^{\infty+i\beta} d\xi \int_{-\infty+i\beta'}^{\infty+i\beta'} d\eta \left(-\frac{2i\xi}{\hbar}\right) \frac{1}{\xi + \frac{\eta}{2}} \frac{1}{\xi - \frac{\eta}{2}}$$

* We neglect the exception of $O(1/2)$.

$$\frac{1}{\xi + \left(\frac{\eta}{2} - \varepsilon_1\right)} \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon_1\right)} \frac{1}{\xi - \left(\frac{\eta}{2} - \varepsilon_1\right)}\quad (7.7)$$

The typical diagram corresponding to this contribution is shown in Fig. 11 (b), in which the particle lines confined in one side of the $\rho(o)$ -line must be all replaced by heavy lines. In carrying out the integration with respect to ξ , we may deform the path of integration into a closed contour by adding a half circle of infinitely large radius in the lower half of the complex plane. Then it can be seen that any pole in the contour is of first degree, since all $0, \varepsilon_1, \varepsilon_2$, are different two by two. Further, by putting $\beta' > 0$, we find that the

only poles at $\xi = \left(\frac{\eta}{2} - X\right)$ contribute after the integration over η , where the contour is again formed in a closed one by adding an infinite half circle. Then as the result of integration with respect to η , we get

$$\begin{aligned}i\lambda^3 \left[\frac{1}{\hbar} \frac{1}{\varepsilon_1 \varepsilon_1 - \varepsilon_2} \{ \exp(-i\varepsilon_1 t/\hbar) - \exp(-i\varepsilon_2 t/\hbar) \} \right. \\ \left. + \frac{1}{\varepsilon_1 \varepsilon_2} \{ \exp(i\varepsilon_1 t/\hbar) - \exp[i(\varepsilon_1 - \varepsilon_2)t/\hbar] \} \right]\end{aligned}$$

For any diagram which is not symmetrical with respect to the $\rho(o)$ -line, there exists a mirror conjugate diagram relative to the $\rho(o)$ -line and the contribution of such a diagram is just the complex conjugate of that of the original diagram. Then adding the contribution of the mirror conjugate diagram to the above result, we get

$$\begin{aligned}\frac{2\lambda^3}{\hbar} \left[\frac{1}{\varepsilon_1(\varepsilon_2 - \varepsilon_1)} \{ \sin(\varepsilon_2 t/\hbar) \} - \sin(\varepsilon_1 t/\hbar) \right] \\ + \frac{1}{\varepsilon_1 \varepsilon_2} \{ \sin[(\varepsilon_1 - \varepsilon_2)t/\hbar] - \sin(\varepsilon_1 t/\hbar) \} \quad (7.8)\end{aligned}$$

After we carry out the summation over ε_1 and ε_2 , this expression can be different from zero only when $\varepsilon_1 < \hbar/t$. This ensures the conservation of unperturbed energy between the initial and the final states. Further, for $\varepsilon_2 < \delta_v E$, $\delta_p E$, the above expression also cancels out as will be seen by putting

$$\varepsilon_1 - \varepsilon_2 = \varepsilon'_2$$

in the first part of the square bracket of (7.8). Thus only non-zero contribution to (7.8) comes from the part

$$\varepsilon_1 < \hbar/t, \quad \varepsilon_2 \gtrsim \text{Min.} \{ \delta_v E, \delta_p E \}$$

in which (7.4) becomes approximately

$$-4\left(\frac{\lambda}{\hbar}\right)^3 \frac{\hbar}{\varepsilon_2} \frac{\hbar}{\varepsilon_1} \sin \varepsilon_1 t / \hbar \sim -4\left(\frac{\lambda}{\hbar}\right)^3 \frac{\hbar}{\varepsilon_2} \delta\left[\frac{\varepsilon_1}{\hbar}\right]$$

Thus transition rate becomes independent of time asymptotically, and hence gives the usual collision factor of the master equation in the time subject to the inequalities (7.1), provided that the transition rate is positive definite.

Let us now show that the contribution of the b -type diagrams is small by the factor τ_0/t or τ_p/t compared to that of the a -type diagrams, of which the justification we have not yet given.

The fact that the time integral over t_1-t_1' , $t_2, t_3, \dots, t_2', \dots, t_9'$ in the $\frac{d}{dt} \sigma_{\Gamma^{(n)}}(n-n'; t)$ gives the time-independent result shows that this time integral is contributed only from the small values of these time variables, not much larger than τ_0 and τ_p . In terms of the original time variable used in Eq. (7.2), this means that the time integrations are non-vanishing only when all t 's and t' 's are almost equal to a certain value, t_r . This is in general true for the contribution of any irreducible linked diagram. For $\sigma_{\Gamma^{(n)}}(n-n'; t)$, the time t_r may have any value between 0 and t and the integration with respect to t_r gives the value proportional to t , while for $\frac{d}{dt} \sigma_{\Gamma^{(n)}}(n-n'; t)$

the time t_r should be practically equal to t . For example, in the case of the diagram of Fig. 5, t_{r1} is practically equal to t , since the contribution of Γ_1 to $\frac{d}{dt} \sigma_{\Gamma^{(n)}}(n-n'; t)$ is considered. On the other hand, the time t_{r2} may assume any value between 0 and t_{r1} for the a -type diagrams, while for the b -type diagrams it can take only value almost equal to t_{r1} . It is now clear that the b -type diagrams contribute $O(1/t)$ compared with the a -type ones. Generality of this proof is evident by the definition of a - and b -type diagrams.

Finally we shall mention of the relation of our results to the non-markoffian equation of Van Hove.¹⁾ As has been shown by Van Hove, the system obeys the non-markoffian equation during the period not so long after the initial setting of the ensemble. In our case, the contribution of the b -type diagrams have been neglected as the quantity of $O(1/t)$. However, it is valid only for sufficiently long time after initial setting of the ensemble. If t is not so large, our derivation of the master

equation may not be legitimated, since some of the b -type diagrams have not their complementary diagrams, and then the temporal behaviour of the system may become non-markoffian.

§ 8. Application to Limiting Cases.

(I) Weak coupling limit. $\lambda \rightarrow 0$, $t \rightarrow \infty$, $\lambda^2 t \sim$ finite.

In this case, the important diagram which contributes to the transition probability in (5.10) is only the second order diagram of Fig. 2, since any linked diagram appeared there gives a contribution of $O(\lambda t)$ and since the first order diagram does not contribute to the transition from n' to n , unless n' is identical with n . The substitution of this result to (5.10) gives the usual master equation based on the Born approximation,⁸⁾

$$\begin{aligned} \frac{d}{dt} \langle n | \rho(t) | n \rangle &= \frac{1}{8\Omega^2} \left(\frac{\lambda}{\hbar} \right)^2 \sum_{KK'k} |v(k)|^2 n_{K+k} n_{K'-k} \\ &\times (1-n_K)(1-n_{K'}) \\ &\times \delta_{KK'} \left[\frac{1}{\hbar} \{ \varepsilon_{K+k} + \varepsilon_{K'-k} - \varepsilon_K - \varepsilon_{K'} \} \right] \\ &\times \{ \langle \dots, n_K+1, n_{K'}+1, n_{K+k}-1, n_{K'-k}-1, \\ &\dots | \rho(t) | \dots, n_K+1, n_{K'}+1, n_{K+k}-1, \\ &n_{K'-k}-1, \dots \rangle - \langle n | \rho(t) | n \rangle \} \end{aligned} \quad (8.1)$$

(II) Low density limit. $C=N/\Omega \rightarrow 0$, $t \rightarrow \infty$, $Ct \sim$ finite.

In this case, the most important diagrams are those which have the least number of particle lines pointing to right, since each rightward particle line contributes $O(C)$ as compared to the leftward one. These diagrams are, as is well known, ladder-type diagrams as illustrated in Fig. 12. The total

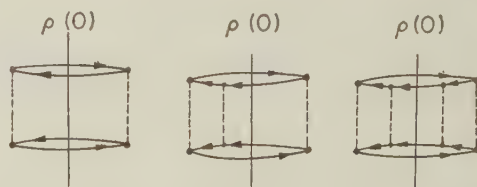


Fig. 12. Simple examples of ladder type diagrams

contribution of these diagrams to the transition probability gives the collision factor at binary collision approximation, since, if we consider a two particle system, the only diagrams which give non-vanishing contribution to the transition probability of (5.10) are also the ladder type diagrams. Then the resulting master equation agrees with Prigogine and Résibois' one.⁹⁾

It should be added that the errors of $O(C)$ come not only from the usual ternary collision terms, but also from the contribution of the n -type diagrams neglected in deriving (5.10). The latter corresponds to the error from the effectively ternary collisions which are included in the successive binary collisions. This result gives the complete correspondence to the result of Brout for low density classical gases.¹⁰⁾

Acknowledgement

The author wishes to express his sincere thanks to Prof. S. Ono at the University of Tokyo for his continued guidance and encouragement throughout the course of this work. He is also grateful to Mr. T. Shizume of Musashi Institute of Technology, Tokyo, for his kind help and fruitful discussions. A part of this work was supported by the Scientific Research Expenditure of the Ministry of Education.

Appendix

In this appendix we generalize some of the discussions of the text to the off-diagonal element of the density matrix, $\langle n' | \rho(t) | n \rangle$, giving in addition some supplementary proofs which are not given in the text. In terms of diagrams, off-diagonal elements can be represented by those which have external lines, while diagonal elements are represented by vacuum diagrams. By an external line we mean a particle line which runs from or towards the edge of the diagram. To make correspondence between the diagram and the contribution to the matrix element $\langle n' | \rho(t) | n \rangle$, we must first generalize the Wick's theorem of §3 in the form which is applicable also to the off-diagonal element. This brings us first to the questions which state we should take as the reference state and what contribution should be represented by an external line. The answer to these questions are, however, simple and as follows. If we take as the reference state the initial state n , then any off-diagonal element can be represented by the diagrams whose external lines all run from or towards the left edge of the diagram and the contribution corresponding to a leftward external line is $(1-n_K)a_K^\dagger$ and to a rightward one $n_K a_K$. These contributions $(1-n_K)a_K^\dagger$ and $n_K a_K$ correspond, in electron-hole language, to the creation of an electron and a hole,

respectively. Since we have taken the initial state n as the reference state, or in other words, as the vacuum state, it is evident that there appears no external line which corresponds to the annihilation of an electron or a hole.

Then Wick's theorem in generalized form can be written as follows:

$$\begin{aligned} \langle n' | \alpha_1 \alpha_2 \cdots \alpha_p | n \rangle = & \langle n' | [: \tilde{\alpha}_1 \cdots \tilde{\alpha}_p : \\ & + : \dot{\alpha}_1 \dot{\alpha}_2 \tilde{\alpha}_3 \cdots \tilde{\alpha}_p : + \cdots + : \dot{\alpha}_1 \tilde{\alpha}_2 \cdots \tilde{\alpha}_{p-1} \dot{\alpha}_p : \\ & + \cdots + : \dot{\alpha}_1 \dot{\alpha}_2 \cdots \tilde{\alpha}_r \cdots \tilde{\alpha}_s \cdots \tilde{\alpha}_t \cdots \tilde{\alpha}_p : + \cdots] | n \rangle \end{aligned} \quad (A.1)$$

where

$$\begin{aligned} \tilde{\alpha}_K = & n_K a_K, \quad \text{for } \alpha_K = a_K \\ = & (1-n_K) a_K^\dagger, \quad \text{for } \alpha_K = a_K^\dagger \end{aligned} \quad (A.2)$$

and in the right hand side we take the whole sum over all possible combinations of contractions and creation operators of electrons or holes. The definition of each term in the r.h.s. is, for example, as follows:

$$\begin{aligned} & : \alpha_1 \alpha_2 \alpha_3 \cdots \alpha_q \cdots \alpha_r \cdots \alpha_s \cdots \alpha_{p-1} \alpha_p : \\ = & (-1)^P (\dot{\alpha}_1 \dot{\alpha}_2) (\dot{\alpha}_3 \dot{\alpha}_4) \cdots (\dot{\alpha}_r \dot{\alpha}_{p-1}) \tilde{\alpha}_2 \cdots \tilde{\alpha}_p \end{aligned} \quad (A.3)$$

where $(-1)^P$ again stands for $+1$ or -1 according as the permutation between the l.h.s. and the r.h.s. is even or odd.

Let us give a brief proof of this theorem, which is of course valid for the special case of the diagonal element in which in the r.h.s. of Eq. (A.1) any term which involves operators $\alpha, \beta, \cdots$ vanishes, since

$$\langle n | \tilde{\alpha} | n \rangle = 0, \quad \tilde{\alpha}_K \tilde{\alpha}_K = \tilde{\alpha}_K \tilde{\alpha}_K^\dagger = 0$$

Proof of (A.1)

If the momenta corresponding to the operators are all different two by two, then the above theorem is evident since $\tilde{\alpha}_K | n \rangle = \alpha_K | n \rangle$ and $\dot{\alpha}_K \hat{\beta}_{K'} \propto \delta_{K'}(K-K')$. This shows that any difference between the l.h.s. and the first term in the square bracket of the r.h.s. of Eq. (A.1) (or we may say any difference between α_K and $\tilde{\alpha}_K$) originates from the product of operators with equal momentum. Then we have only to prove for the case in which all α_j 's ($j=1, 2, \cdots, p$) have the same wave number K . We give the proof for such product, distinguishing into two cases.

(I) For $A_K \alpha_K \alpha_K B_K$: where A_K, B_K represent the products of α_K and $\alpha_K^\dagger$, $\alpha_K^\dagger$ being the self-adjoint operator of α_K . In this case, the l.h.s. of (A.1) always vanishes and the r.h.s. is also seen to vanish from

$$\begin{aligned} \tilde{\alpha}_K \tilde{\alpha}_K &= 0 \\ \tilde{\alpha}_K (\dot{\alpha}_K \dot{\alpha}_K^\dagger) &= n_K (1-n_K) \alpha_K = 0 \end{aligned}$$

$$\begin{aligned}
&:\dot{\alpha}_K+\dot{\alpha}_K\tilde{\alpha}_K: + : \dot{\alpha}_K\tilde{\alpha}_K\dot{\alpha}_K: = 0 \\
&(\dot{\alpha}_K+\dot{\alpha}_K)(\dot{\alpha}_K\dot{\alpha}_K^+) = n_K(1-n_K) = 0 \\
&:\dot{\alpha}_K\dot{\alpha}_K\dot{\alpha}_K^+ + \dot{\alpha}_K^+: + : \dot{\alpha}_K\dot{\alpha}_K\dot{\alpha}_K^+\dot{\alpha}_K^+: = 0
\end{aligned}$$

The reader will have noticed that the last equation shows the existence of the complementary diagram for any diagram of the type described in Fig. 5 (c) and (e) of §5.

(II) For $\alpha_K\alpha_K^+\alpha_K\alpha_K^+\dots$: Let us denote the r.h.s. of Eq. (A.1) which corresponds to such product by $\langle n'|A_K^{(p,q)}|n\rangle$, where p and q stand for the number of α_K and α_K^+ respectively and $|p-q|\leq 1$. For $p=1$,

$$A_K^{(1,0)} = \tilde{\alpha}_K = \alpha_K = \text{l.h.s.}$$

$$A_K^{(1,0)} = \tilde{\alpha}_K\tilde{\alpha}_K^+ + \dot{\alpha}_K\dot{\alpha}_K^+ = \alpha_K\alpha_K^+ = \text{l.h.s.}$$

For any value of p

$$A_K^{(p,p-1)} = \tilde{\alpha}_K A_K^{(p-1,p-1)} + \dot{\alpha}_K\dot{\alpha}_K^+ A_K^{(p-1,p-2)}$$

$$= \tilde{\alpha}_K A_K^{(p-1,p-1)} = \alpha_K A_K^{(p-1,p-1)}$$

$$A_K^{(p,p)} = \alpha_K\alpha_K^+ A_K^{(p-1,p-1)} = \alpha_K A_K^{(p-1,p)}$$

using the result of (I) and noting that $A_K^{(p,p)}$ is a pure number. Then our theorem is proved by induction.

Then the one-to-one correspondence between Feynman diagrams and the contribution to $\langle n'|\rho(t)|n\rangle$ is evident and we have only mention that to the external line corresponds to the creation operator of an electron or a hole according as it points to left or right. The summation over the wave numbers of the external lines, however, should be made for each line only over the values which give the different values between n_K and n_K' .

The linked cluster expansion is also applicable to diagrams which have external lines, since any linked diagram has even number of external lines on account of the conservation of the particle number throughout the interaction, so that the $\sigma_L^{(n)}$ -operators corresponding to such diagrams are as yet commutable each other. Then we get, after performing the linked cluster expansion

$$\langle n'|\rho(t)|n\rangle = \langle n'|\sigma_{na}^{(n)}(t) \exp[\sigma_L^{(n)}(t)]\rho(0)|n\rangle \quad (\text{A.4})$$

where $\sigma_{na}^{(n)}(t)$ is the $\sigma_L^{(n)}$ -operator corresponding to the contribution of the diagrams with external lines.

Finally, let us make the order estimation for the contribution of a given linked diagram.

First, each interaction involves $1/\mathcal{Q}$, as is seen from Eq. (2.3), so that if there are ν interaction lines they contribute $\mathcal{Q}^{-\nu}$. The contribution of an interaction line also involves a product of three Kronecker's deltas and it gives a restriction on the wave numbers of the particle lines. If we ignore these Kronecker's deltas, each of the summations over the wave numbers of the intermediate particle lines which connect between vertices gives $O(\mathcal{Q})$ and they contribute as a whole $\mathcal{Q}^p$, where p is the number of such particle lines. However, as there are $(\nu-1)$ independent δ_{kr} 's, the contribution of a linked diagram becomes as a total

$$\mathcal{Q}^{-\nu}\mathcal{Q}^{p-(\nu-1)} = \mathcal{Q}^{1-q} \quad (\text{A.5})$$

where q is the half number of the external lines and we have used the relation

$$p+q=2\nu$$

The above order estimation shows that any linked vacuum diagram contributes $O(\mathcal{Q})$ while that with external lines $\mathcal{Q}^{-1}$, $\mathcal{Q}^{-2}$, $\dots$, since each linked diagram except the vacuum diagram should have at least four external lines.

Then we find from (A.4) that the off-diagonal element of the density matrix is always smaller than the diagonal element at least by $O(\mathcal{Q})$.

References

- 1) L. Van Hove: *Physica* **23** (1957) 441.
- 2) R. P. Feynman: *Phys. Rev.* **76** (1949) 749. see also S. S. Schweber, H. A. Bethe and F. de Hoffmann: *Mesons and Fields*, Vol. **1** (Row, Peterson, 1956).
- 3) G. C. Wick: *Phys. Rev.* **80** (1950) 268.
- 4) R. C. Tolman: *Principles of Statistical Mechanics* (Oxford, 1939).
- 5) I. Prigogine and S. Ono: *Physica* **25** (1959) 171.
- 6) J. Goldstone: *Proc. Roy. Soc. A*, **239** (1957) 267.
- 7) C. Bloch: *Nucl. Phys.* **7** (1958) 451.
- 8) L. Van Hove: *Physica* **21** (1955) 517.
- 9) I. Prigogine and P. Résibois: *Physica* **24** (1958) 795.
- 10) R. Brout: *Physica* **22** (1956) 509.
- 11) J. Hubbard: *Proc. Roy. Soc. A*, **240** (1957) 539.
- 12) N. M. Hugenholtz: *Physica* **23** (1957) 533.

Annealing of γ -Ray Damage in Germanium

By Tsunesaburo ASADA, Haruo SAITO,
Kazumi OMURA, Taiji OKU

*Department of Physics, Faculty of Science,
Osaka University*

and Masahiro OKA

*Department of Physics, Liberal Arts College,
Shimane University*

(Received August 6, 1959)

Isothermal annealing of germanium single crystals irradiated by γ -rays from Co 60 was studied. The variation of conductance with time was measured. The conductance curves are composed of three stages. To explain this fact, the model proposed by Fletcher and Brown may be employed with a certain modification. From the analysis of these curves, the activation energy of the direct recombination of vacancy interstitial pairs, that for the diffusion of interstitial atoms and that for the diffusion of vacancies were determined to be 0.765 eV., 0.741 eV. and 1.250 eV., respectively.

Annealing of germanium single crystals irradiated by γ -rays from Co 60 at a temperature range of 0–55°C was studied. Conductivity variation was observed which may be attributable to the preferential annealing of interstitial atoms followed by the annealing of vacancies.

Specimens about $1 \times 1 \times 5 \text{ mm}^3$ were cut from a single crystal of n-type germanium which had initially a resistivity of 15 ohm-cm at room temperature.

The specimens were exposed to γ -rays from

stant temperatures in the range from 10°C to 55°C. The variation of resistance with time was measured. Typical curves showing the relations between the conductance of the specimens and annealing time interval at constant temperatures are shown in Fig. 1. During the course of annealing, the conductance increased at the initial stage, then decreased to a certain value and again increased asymptotically to a final value σ_0 .

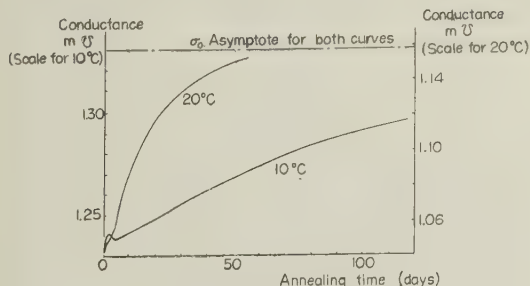


Fig. 1. Conductance of specimens vs annealing time.

1500 Curie Co 60 to a total dose of $4 \times 10^7 \text{ r}$ at -77°C . The resistivity was observed to increase by about 25%¹⁾.

After it was confirmed that remarkable resistivity change did not occur during the preservation of the irradiated specimens below -20°C , isothermal annealing of these specimens was carried out at predetermined con-

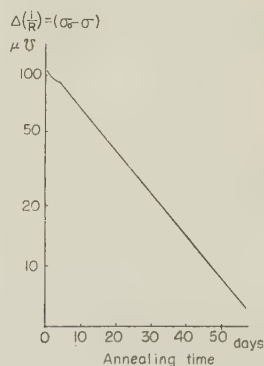


Fig. 2. Plot of $(\sigma_0 - \sigma)$ vs annealing time.

It was found that the last stage of annealing may be represented by $A(1 - \exp(-t/\tau_3))$. In order to obtain the time constant τ_3 , the values of $\log(\sigma_0 - \sigma)$ were plotted against time, σ being the conductance of the specimens during the annealing. The result is shown in Fig. 2 and it can be represented by a fairly good straight line except for the initial stage.

On closer examination of the deviation from linearity it was concluded that the conductance can be represented as

$$\frac{1}{R} = \frac{1}{R_0} - k_1 e^{-t/\tau_1} + k_2 e^{-t/\tau_2} - k_3 e^{-t/\tau_3} \quad (1)$$

The constants τ_1 , τ_2 and τ_3 can be easily estimated by the graphical method. Their values are given in Fig. 3.

To explain the fact that the conductance curve consists of three stages Fletcher and Brown's interpretation^{2),3)} for annealing process was employed with a slight modification. It is well known that vacancies act as ac-

annealing temperature, direct recombination of a vacancy with an interstitial atom in each pair may occur in the first stage. This is simply an annihilation of pairs and the amount annealed may be represented by a simple exponential form with a time constant τ_1 .

The so-called "reverse annealing" stage, in which σ decreases with a time constant τ_2 , may be considered as follows⁴⁾⁻⁶⁾. When the specimens are heated, direct recombination may occur as described above. One component of the Frenkel defects, presumably the interstitial atoms, will begin to diffuse faster than the vacancies. Once liberated from the vacancies, they will wander in the crystal lattice and will finally be annihilated at dislocations or at the surface. This process may have a longer relaxation time than the direct recombination process. When these interstitial atoms disappear at dislocations or at the surface, σ may decrease, because they are acting the role of donors in the crystal.

After the preferential annealing by these mechanisms is over the vacancies left in the crystal may wander about in the crystal and be annihilated at dislocations or surfaces with a time constant τ_3 .

If this model is adopted, analysis of the curves shown in Fig. 3 gives following values for the activation energies in the three stages; the activation energy for the direct recombination of vacancy interstitial pairs, 0.765 ± 0.004 eV., that for the diffusion of the interstitial atoms, 0.741 ± 0.001 eV., and that for the diffusion of the vacancies, 1.250 ± 0.001 eV.

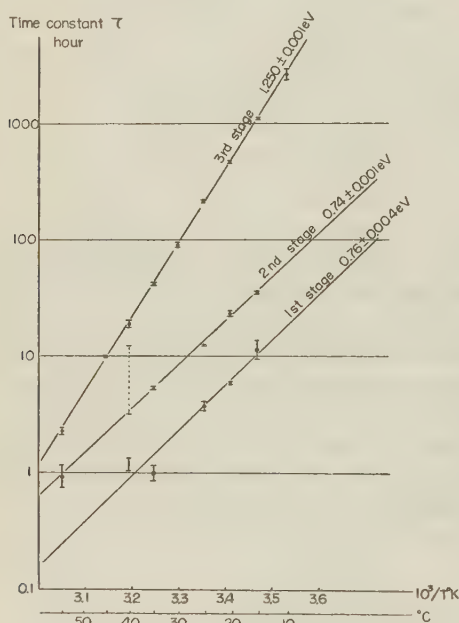


Fig. 3. Plot of τ vs $1/T$.

ceptors, whereas interstitial atoms act as donors. In n-type germanium used for our experiments a lattice vacancy can trap two electrons from conduction band and an interstitial atom supplies one to conduction band. In the present investigation the concentration of vacancy interstitial pairs is estimated to be of the order of $10^{13}/\text{cc}$, from the difference in resistivity before and after irradiation. In such a case it is almost evident that the vacancy interstitial pairs lie far apart from each other compared with the distance in each pair. When the specimens are heated to an

References

- 1) J. W. Cleland, J. H. Crawford, Jr. and D. K. Holmes: Phys. Rev. **102** (1956) 722.
- 2) R. C. Fletcher and W. L. Brown: Phys. Rev. **92** (1953) 585.
- 3) W. L. Brown, R. C. Fletcher and K. A. Wright: Phys. Rev. **92** (1953) 591.
- 4) J. W. Cleland, J. H. Crawford, Jr. and J. C. Pigg: Phys. Rev. **99** (1955) 1170.
- 5) J. H. Crawford, Jr. and J. W. Cleland: *Progress in Semiconductors*, vol. **2**, (John Wiley and Sons, N. Y.)
- 6) J. W. Cleland and J. H. Crawford: J. Appl. Phys. **29** (1958) 149.

A.C. and D.C. Field Effects on Cleaned Germanium Surfaces*

By Shinji KAWAJI

*Department of Physics and Chemistry, Gakushuin University
Mejiro, Tokyo*

(Received September 5, 1959)

Measurements of the a.c. and d.c. field effects were made on the conductance of the germanium surfaces cleaned by Joule heating up to about 800°C in ultra-high vacuum. In the measurements of the a.c. field effect on the cleaned surface, the minimum of conductance showing the surface was slightly *n*-type was observed and the density of fast states was estimated at $1.7 \times 10^{13}/\text{cm}^2 \cdot \text{volt}$. When the surface was exposed to oxygen, the fast state density decreased down to $2.4 \times 10^{12}/\text{cm}^2 \cdot \text{volt}$ and the surface potential decreased by 0.03 volts. These results suggest that the fast states are dangling bonds at the surface. In the measurements of the d.c. field effect on the cleaned surface, the slow decay of the changes in conductance was not recognized. The slow decay appeared when the surface was exposed to air. These results show that the slow states are attributed to adsorbed gases on the outer surface of the oxide layer of germanium.

§ 1. Introduction

Considerable progress^{1)~20)} has been made recently in understanding the physical properties of the so-called "real surface" of germanium. It is now quite clear that two types of surface states having different time constants to reach equilibrium with the interior, "fast states" and "slow states", exist on a germanium real surface.^{4)~7) 11)} The fast states, having the time constant of the order of microsecond or less,⁴⁾⁶⁾⁷⁾ are responsible for surface recombination of holes and electrons and considered to be located at the interface between the surface oxide layer and germanium proper. According to the investigations of several workers,^{8)~16)} the fast states are acceptor levels and their density is about $10^{11} \sim 10^{12}$ per cm^2 . Recent development²¹⁾²²⁾ of the study on "cleaned surfaces" suggests that the fast states are Tamm-like levels. The time constants of the slow states vary from seconds to hours strongly depending on ambient gases and the oxide thickness.⁴⁾⁶⁾¹⁷⁾¹⁸⁾ Thus the slow states are considered to be located on the outer surface of the oxide layer, and their origin seemed to be attributed to adsorbed gases.¹⁹⁾

The experiments to be reported here were designed to find more evidence for the models of the origin of surface states accepted at

present by means of the measurements of field effect for cleaned surfaces and its change with the exposure to oxygen or air. The procedure to obtain the cleaned surface was heating the crystal up to 800°C in ultra-high vacuum. The measurements involve (A) a.c. field effect: the measurements of change in conductance with alternating transverse field for the study of fast states, (B) d.c. field effect: the measurements of change in conductance and its relaxation effect with d.c. transverse field for the study of slow states.

§ 2. Experiments

(A) a.c. field effect

The sample used was an etched slice of 40 ohm-mm *n*-type germanium single crystal $0.5 \times 2.5 \times 10 \text{ mm}^3$, which was mounted on the sample holder shown in Fig. 1. The measured surface was a (111) plane of the crystal. Spacing between the crystal surface and the field effect probe was about 0.07 mm. a.c. field effect was measured using a 50 cps field from peak to peak 4×10^5 volts/cm. The circuit used was similar to Montgomery and Brown's.⁸⁾

The sample holder was sealed in a glass test tube which was connected to high vacuum system shown in Fig. 2. After the sample stood in hydrogen gas at pressure about 5 cm Hg at 500°C for 24 hours in order to reduce the germanium surface, the system was evacuated to 10^{-7} mmHg at 500°C for 24 hours

* This paper is presented as partial fulfillment of the requirements for the degree of Doctor of Science in Physics at the Hokkaido University.

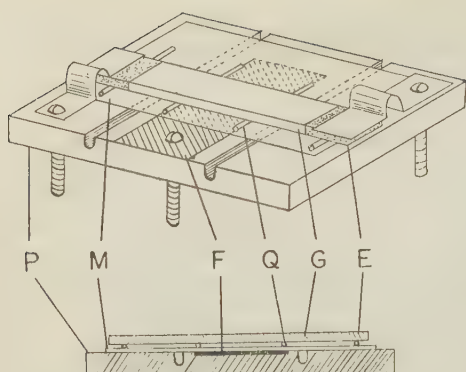


Fig. 1. The sample holder. P: quartz plate; M: mica sheet; F: field effect probe of evaporated chromium film; Q: quartz rod; G: germanium slice; E: evaporated chromium electrode.

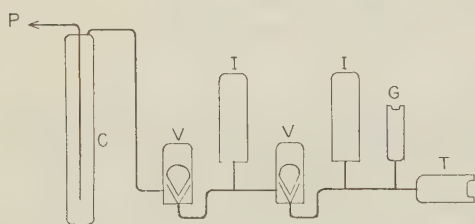


Fig. 2. The vacuum system. P: to oil diffusion Hickmann pump and gas reservoir; V: glass ground valve operated magnetically without grease; I: Alpert's ionization gauge; G: titanium getter; T: test tube; C: cold trap.

in an oven. During this evacuation, the filament of Alpert's ionization gauge, the titanium getters and the germanium slice were out-gassed by passing a.c. current through them. Soon after the oven was taken away, the trap was immersed into a liquid nitrogen bath, glass ground valves without grease were shut and ionization gauges and getters were operated, then the sample was heated up to 800°C for ten minutes by passing a.c. current through it. The sample cooled to room temperature, in 20 minutes after the heating current was switched off, then measurements were performed. The pressure during measurements was maintained at 10^{-9} mmHg. After the measurements for this cleaned surface was carried out, oxygen gas was introduced into the vacuum system up to few mmHg. After the sample was exposed to oxygen atmosphere for one minute, the system was evacuated again to the pressure lower than 10^{-6} mmHg in order to avoid the discharge by

gases between the sample and the field effect probe, and then measurements was performed for this oxidized surface. In above mentioned cleaning process, the sample was converted to 40 ohm-cm *p*-type due to the creation of thermal acceptors by heat-treatment.

The measured a.c. field effect patterns for the cleaned and the oxidized surfaces are shown in Fig. 3. Curve (1) shows the theoretical conductance change³⁾ versus induced surface charge density by transverse electric field in the case of no surface states. ϕ_s is the position of the Fermi level at the surface measured with respect to the Fermi level in intrinsic material, thus, $\phi_s > 0$ means that the surface is *n*-type and $\phi_s < 0$ means that the surface is *p*-type. Curve (2) shows changes in conductance for the cleaned surface and curve (3) shows changes in conductance for the oxidized surface. In this figure the minimum points of experimental patterns are shifted so as to coincide with the minimum point of theoretical one. This may be allowed since on these surface it has been confirmed by d.c. field effect that the slow states do not exist.

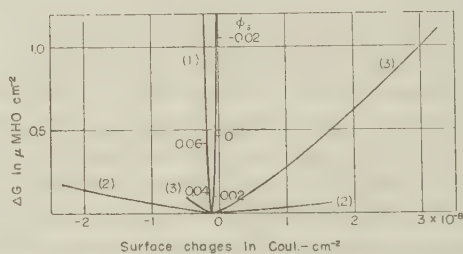


Fig. 3. Measured field effect patterns compared with the theoretical change in conductance. Curve (1): theoretical conductance change versus induced surface charge density in the case of no surface states. ϕ_s is the position of the Fermi level at the surface measured with respect to the Fermi level in intrinsic material. Curve (2): the field effect pattern of the cleaned surface. Curve (3): the field effect pattern of the oxidized surface.

(B) d.c. field effect

Slow decays of d.c. field effect were measured by d.c. bridge circuit with a galvanometer whose period was 2 sec and sensitivity was 10^{-10} amp/div. The sample, etched slice of *n*-type 40 ohm-cm single crystal, was mounted on the same type holder shown in Fig. 1.

The sample was cleaned by Joule heating

in ultra-high vacuum similarly to the case of the a.c. field effect experiment. In this case, the sample was heated up to 750°C for 20 minutes, then allowed to cool to room temperature at the free radiation rate. The pressure was 3×10^{-8} mmHg after this procedure. The resistivity of the sample was changed to *p*-type 12 ohm-cm owing to the creation of thermal acceptors due to this heat-treatment. 20 minutes after the heating current of the sample was switched off, a.c. field effect pattern showed the surface was *p*-type and field effect mobility was 5.8 cm²/volt-sec. We could not measure d.c. field effect for one hour after the Joule heating because of the gradual change in the resistance due to change in the temperature of the sample. The changes in the conductance of the cleaned sample by d.c. transverse field are shown in Fig. 4. Fig. 4 (a) was measured one hour after the Joule heating of the sample, and Fig. 4 (b) was measured 40 minutes later than measurement (a). The field effect mobility is 77 cm²/volt-sec, and 102 cm²/volt-sec respectively, in Fig. 4 (a) and Fig. 4 (b). We can not recognize slow decay of the d.c. field effect in Fig. 4 (a).

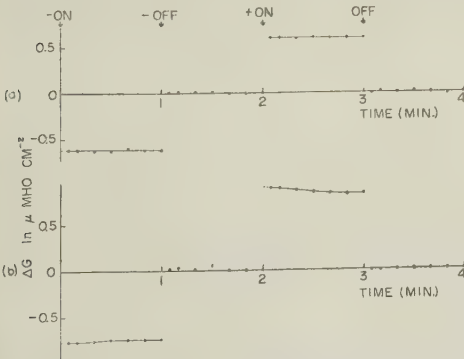


Fig. 4. The changes in conductance of the cleaned surface by d.c. transverse field; (a): measured one hour after the heating current was switched off, (b): measured 40 minutes later than measurement (a). Charges of $\pm 8 \times 10^{-9}$ coulombs/cm² are induced on the germanium surface respectively at the arrows (+on) and (-on), and the fields were switched off at the arrow (off).

In Fig. 4 (b) the slow decay cannot be recognized appreciably. After the measurements for the cleaned surface was carried out, the air was introduced into the test tube and then evacuated up to 10^{-6} mmHg immediately. The slow decay of d.c. field effect slightly appeared as shown in

Fig. 5 (a). Then the air was again introduced into the test-tube, the slow decay was observed as shown in Fig. 5 (b). In this figure, for the convenience of comparison, the value of ΔG at $t=0$ for curve (a) is taken equal to that for curve (b). The test tube was evacuated again to 10^{-6} mmHg, the slow decay much the same as Fig. 5. (a) was observed again. It is found that the surface changes to *n*-type after exposing to air.

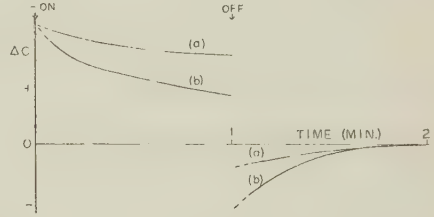


Fig. 5. The relative slow decay curves of d.c. field effect; (a): exposed to air and evacuated subsequently, (b): exposed to air.

§ 3. Discussion

In Fig. 3, the total surface charge density Σ_T consists of a portion Σ_{sc} in the space charge layer, which contribute to the conductance, and the other portion Σ_s which is trapped in surface states. The theoretical curve (1) relates to changes in conductance per unit area of surface ΔG versus Σ_{sc} . The experimental curve relates to ΔG versus Σ_T . From the curve (2) in Fig. 3 it is found that ϕ_s of the cleaned surface is 0.03 volts showing the surface is slightly *n*-type. Since the minimum in conductance was observed in the experimental curve, values of Σ_{sc} and ϕ_s can be determined for any value of conductance, then the relation between $\Sigma_s = \Sigma_T - \Sigma_{sc}$ and ϕ_s can be determined for any observed values of ΔG . If we could obtain the relation between Σ_s and ϕ_s for a large range in ϕ_s , we would estimate the density of surface states and their distribution in energy. Since we could only measure the relation between Σ_s and ϕ_s for the limited range in ϕ_s in this experiment, the density of surface state per volt of surface potential was estimated to be $\partial(\Sigma_T - \Sigma_{sc})/\partial\phi_s$. The estimated density of fast states are $1.7 \times 10^{13}/\text{cm}^2 \cdot \text{volt}$ for the cleaned surface and $2.4 \times 10^{12}/\text{cm}^2 \cdot \text{volt}$ for oxidized surface. The surface potential, defined as the difference of the electrostatic potential at the surface from its bulk value, of the cleaned surface decreased by 0.03 volts

with introduction and successive evacuation of oxygen.

The result that the fast states density decreases by one order of magnitude due to adsorption of oxygen appears to show that the fast states we measured are dangling bonds at the surface of germanium proper and oxygen is adsorbed by making covalent bonds with unpaired electrons on the cleaned surface. But, in order to explain the fact that the cleaned surface is slightly *n*-type, or, the surface is charged positively to 3×10^{-10} coulombs/cm², we must consider the existence of some positively charged centers at or near the surface. In the case of d.c. field effect experiments the cleaned surface is *p*-type but not strongly. As mentioned in the section of d.c. field effect experiments, the surface remained always *p*-type, though the field effect mobility increased with time in vacuum of 3×10^{-8} mmHg showing the decrease of fast state density due to the contamination of residual gases. These results show that the positive surface charges can not be attributed to the contamination of residual gases. If the energy of the acceptor levels attributed to the surface dangling bonds is far lower than the intrinsic Fermi level, it is necessary that the density of ionized donors at the surface is larger than 10^{13} /cm² in order to explain our results. If the energy of the acceptor levels is $5 \sim 7kT$ higher than the intrinsic Fermi level referring to the data for real surfaces, the ionized donors of about 10^{11} /cm² are required to explain our results. The origin of these ionized donors at or near the surface is not well known.

The result that the fast state density of oxidized surface is larger than the value for etched surfaces shows that the surface heated in high vacuum differ from etched surfaces in the surface structure. The measured fast state density of the cleaned surface is much smaller than the density of bonds cut at the (111) crystal plane, 7.3×10^{14} /cm². This may be attributed to that the oxide could not be removed thoroughly by heat-treatment.

Our results that the cleaned surfaces are slightly *n* or *p*-type is different from the results by Handler and others²¹⁾²³⁾²⁴⁾ who reported that the surface cleaned by argon-ion bombardment and subsequent annealing is strongly *p*-type. The surface cleaved in ultra-high vacuum is nearly intrinsic according to

the experiment of Barnes and Banbury,²⁵⁾ but strongly *p*-type according to the experiment of Palmer and Dauenbaugh.²³⁾ In this respect further studies will be needed.

It has been found by several workers that the relaxation time of d.c. field effect depends on oxide thickness¹⁷⁾¹⁸⁾ and surrounding gas ambient.⁴⁾⁶⁾⁷⁾ Hence it is considered that the slow states are attributed to gases adsorbed on the outer surface of the oxide layer of germanium.¹⁹⁾ Our results, that the slow decay in d.c. field effect was not recognized on the cleaned surface as shown in Fig. 4 (a) and appeared only when the sample was exposed to air as shown in Fig. 5, also show the slow states are attributable to adsorbed gases. In Fig. 4 (b), which was measured one hundred minutes after the Joule heating of the sample, slow decay seemed to appear slightly. The increasing of the field effect mobility with time shows that the surface was covered gradually with residual gases and hence fast states decreased even in the high vacuum of 3×10^{-8} mmHg. The result of Fig. 4 (b) seems to show that the number of slow states increases with increasing adsorbed gases. But this is not certain, since the magnitude of the decay is within the limit of the change in conductance due to fluctuation of temperature.

§ 4. Conclusion

By observing a.c. and d.c. field effect for the germanium surfaces cleaned by heating in ultra-high vacuum, it was found that (1) the cleaned surface was nearly intrinsic, (2) the fast state density was decreased with adsorption of oxygen, (3) the slow decay of d.c. field effect could not be recognized on the cleaned surface, (4) the cleaned surface was getting more *p*-type with time even in the vacuum of 10^{-8} mmHg.

Acknowledgement

The author wishes to express his sincere appreciation to Professor Akio Kobayashi and Professor Jiro Huruichi, Hokkaido University, who made many valuable suggestions and discussions and gave helpful encouragement to him during the course of the work. The author is greatly indebted to Professor Juro Horiuchi and members of the Research Institute for Catalysis, Hokkaido University, for many helps in the performance of experiments.

References

- 1) W. Shockley and G. L. Pearson: *Phys. Rev.* **74** (1948) 232.
- 2) W.H. Brattain and J. Bardeen: *Bell Syst. Tech. J.* **32** (1953) 1.
- 3) C.G.B. Garrett and W.H. Brattain: *Phys. Rev.* **99** (1955) 376.
- 4) G.G.E. Low: *Proc. Phys. Soc. London B*, **68** (1955) 10.
- 5) P. C. Banbury, G. G. E. Low and J.D. Nixon: *Semiconductor Surface Physics* (Univ. of Pennsylvania Press, Philadelphia, 1956) 70.
- 6) R. H. Kingston and A. L. McWhorter: *Phys. Rev.* **103** (1956) 534.
- 7) H. C. Montgomery: *Phys. Rev.* **106** (1956) 441.
- 8) H. C. Montgomery and W. L. Brown: *Phys. Rev.* **103** (1956) 865.
- 9) J. Bardeen, R. E. Coovert, S. R. Morrison, J. R. Schrieffer and R. Sun: *Phys. Rev.* **104** (1956) 47.
- 10) W.H. Brattain and C.G.B. Garrett: *Bell Syst. Tech. J.* **35** (1956) 1019. C. G. B. Garrett and W. H. Brattain: *Bell Syst. Tech. J.* **35** (1956) 1041.
- 11) W. L. Brown, W.H. Brattain, C.G.B. Garrett and H.C. Montgomery: *Semiconductor Surface Physics*, Parts 1 and 2, (Univ. of Pennsylvania Press, Philadelphia, 1957) 111.
- 12) S. Wang and G. Wallis: *Phys. Rev.* **105** (1957) 1459.
- 13) H. Statz, G. deMars, L. Davis, Jr. and A. Adams, Jr.: *Phys. Rev.* **106** (1957) 455.
- 14) A. Many, E. Harnick and Y. Margoninski: *Semiconductor Surface Physics* (Univ. of Pennsylvania Press, Philadelphia, 1957) 85.
- 15) A. Many and D. Gerlich: *Phys. Rev.* **107** (1957) 404.
- 16) C.G.B. Garrett: *Phys. Rev.* **107** (1957) 478.
- 17) M. Lasser, C. Wysocki and B. Bernstein: *Semiconductor Surface Physics* (Univ. of Pennsylvania Press, Philadelphia, 1957) 197.
- 18) M. Kikuchi: *J. Phys. Soc. Japan* **12** (1957) 756.
- 19) S.R. Morrison: *Semiconductor Surface Physics* (Univ. of Pennsylvania Press, Philadelphia, 1957) 169.
- 20) A. Many: *J. Phys. Chem. Solids* **8** (1959) 87.
- 21) P. Handler: *Semiconductor Surface Physics* (Univ. of Pennsylvania Press, Philadelphia, 1957) 23.
- 22) A. Kobayashi and S. Kawaji: *J. Phys. Soc. Japan* **12** (1957) 1054.
- 23) R. Missman and P. Handler: *J. Phys. Chem. Solids* **8** (1959) 109.
- 24) S. Wang and G. Wallis: *J. Appl. Phys.* **30** (1959) 285.
- 25) G. A. Barnes and P.C. Banbury: *Proc. Phys. Soc. London B*, **71** (1958) 1021; *J. Phys. Chem. Solids* **8** (1959) 111.
- 26) D. R. Palmer and C. E. Dauenbaugh: *Bull. Amer. Phys. Soc.* **II**, **3** (1958) 138.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 1, JANUARY, 1960

Crystal Structure of Silicon Carbide of 174 Layers

By Takanori TOMITA

Department of Physics, Saitama University, Urawa

(Received July 17, 1959)

A new modification of silicon carbide crystal, having rhombohedral symmetry and a unit cell composed of 174 layers, was found by X-ray study. The cell size and symmetry were determined in a similar way as in a previous study of silicon carbide of 594 layers²⁾. The structure, namely the stacking order of Si-C layers, of the new modification was determined by comparing the visual intensity with those calculated for a number of models. The structure is represented as $\{\text{C}(\text{CCH})_7\text{C}_3(\text{CCH})_{11}\} \times 3$ by Wyckoff's notation¹⁰⁾.

§ 1. Introduction

For silicon carbide crystals, a number of modifications has been found. The modifications are distinguished from each other by

the stacking order of Si-C layers along *c*-axis. The *c*-period sometimes includes as many layers as 594²⁾. Here, a new modification having *c*-period of 174 layers and rhom-

bohedral symmetry is found (section 3).

The new modification is found for many domains on a specimen surface. A fine X-ray source⁶⁾ was applied to resolve the reflections of these domains (section 2).

The structure of silicon carbide crystal is rather simple in respect that every Si-C layer occupies one of three sites, A, B and C of hexagonal base. For the new modification of long period, however, the number of possible orders of stacking in the period of 174 layers of rhombohedral lattice amounts to 2^{57} taking into account that two successive layers do not occur at the same sites of A, B or C. Of these, 50 models were selected, which were suggested from the characteristic feature of the observed intensity distribution (section 4).

The intensities calculated for these models were compared with the visual one, and it was found that the intensity for the structure represented as $\{C(CCH)_7C_3(CCH)_{11}\} \times 3$ by Wyckoff's notation shows the best agreement with the observed intensity.

§ 2. Experimental

The specimen, in which the new modification was found, is an opaque blackish low habit crystal of about $1 \times 2 \times 0.5 \text{ mm}^3$ covered with transparent glassy melt (Fig. 1-c and -d).

Fig. 1-a and -b reproduce the *c*-axis oscillation photographs of the specimen. The main body of the specimen shows the reflections of six-layer period (indicated by **A** in the figure). A thin surface layer of the specimen, shown in Fig. 1-d, gives many series of the reflections of fine intervals corresponding to the new long period (indicated by **B**, **C** and **D**, **E** in the figure). These series show that the specimen surface is composed of many domains. A divergent X-ray beam, from an intense fine source⁶⁾ and through a thin slit parallel to the specimen surface, gives rise to the reflections of different domain at different positions on the film. Of these domains, those giving the reflections **B** and **C** in Fig. 1-b have the same orientations, and those giving **E** in Fig. 1-a show twin orientation relative to the formers. There is also a domain giving diffuse scattering indicated by **F** in Fig. 1-a. The diffuse scattering has maxima at the positions corresponding to those of the reflections due to six-layer

period. Therefore, the structure of the domain probably has a sequence of Si-C layers modulated from the regular six-layer period³⁾.

§ 3. Determination of Cell Size and Symmetry

It is observed in Fig. 1-a and -b that $(10\bar{1}l)$ reflections of the new modification are disposed relative to those of six-layer period as shown schematically in Fig. 2 (b); the reflections $(10\bar{1}1)$ and $(10\bar{1}4)$ of six-layer period coincide respectively with the reflections $(10\bar{1}, 29)$ and $(10\bar{1}, 116)$ due to the new long period, $(10\bar{1}2)$ and $(10\bar{1}5)$ of six-layer period shift in one direction from $(10\bar{1}, 59)$ and $(10\bar{1},$

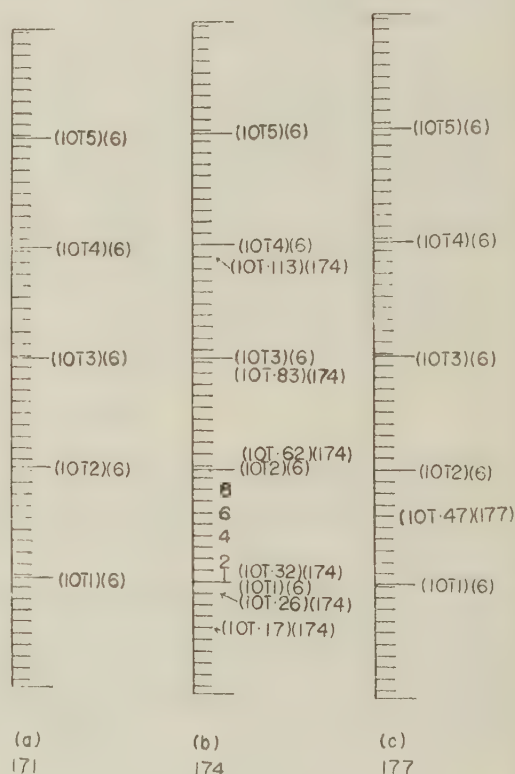


Fig. 2. Distributions of reciprocal $(10\bar{1}l)$ lattice points corresponding to 171, 174 and 177 layers rhombohedral structures relative to those of 6-layer structure.

146) of the new long period, and $(10\bar{1}3)$ shifts by the same distance in the opposite direction from $(10\bar{1}, 86)$. Similar observations of reflections over all $\{10\bar{1}l\}$ lattice rods revealed the rhombohedral symmetry of the modification.

The extinction rule for rhombohedral sym-

metry indicates that the period of reciprocal c -axis of the modification corresponds to one third the way between two successive reflections. The oscillation photographs show that the interval between $(10\bar{1}1)$ and (1012) reflections of six-layer period is equal to nine intervals of the reflections of long period plus the separation of two thirds the way between two successive reflections. Then the number

of layers in one cell should be $6(9 \times 3 + 2) = 174$. Other layer numbers near 174, say 171 or 177, are ruled out, since the dispositions of their reflections relative to those due to six-layer period are evidently different as shown in Fig. 2 (a) and (c).

The cell of the new modification has a c -period as long as $2.51 \times 174 = 436.7 \text{ \AA}$ and three rhombohedral units of 58 layers.

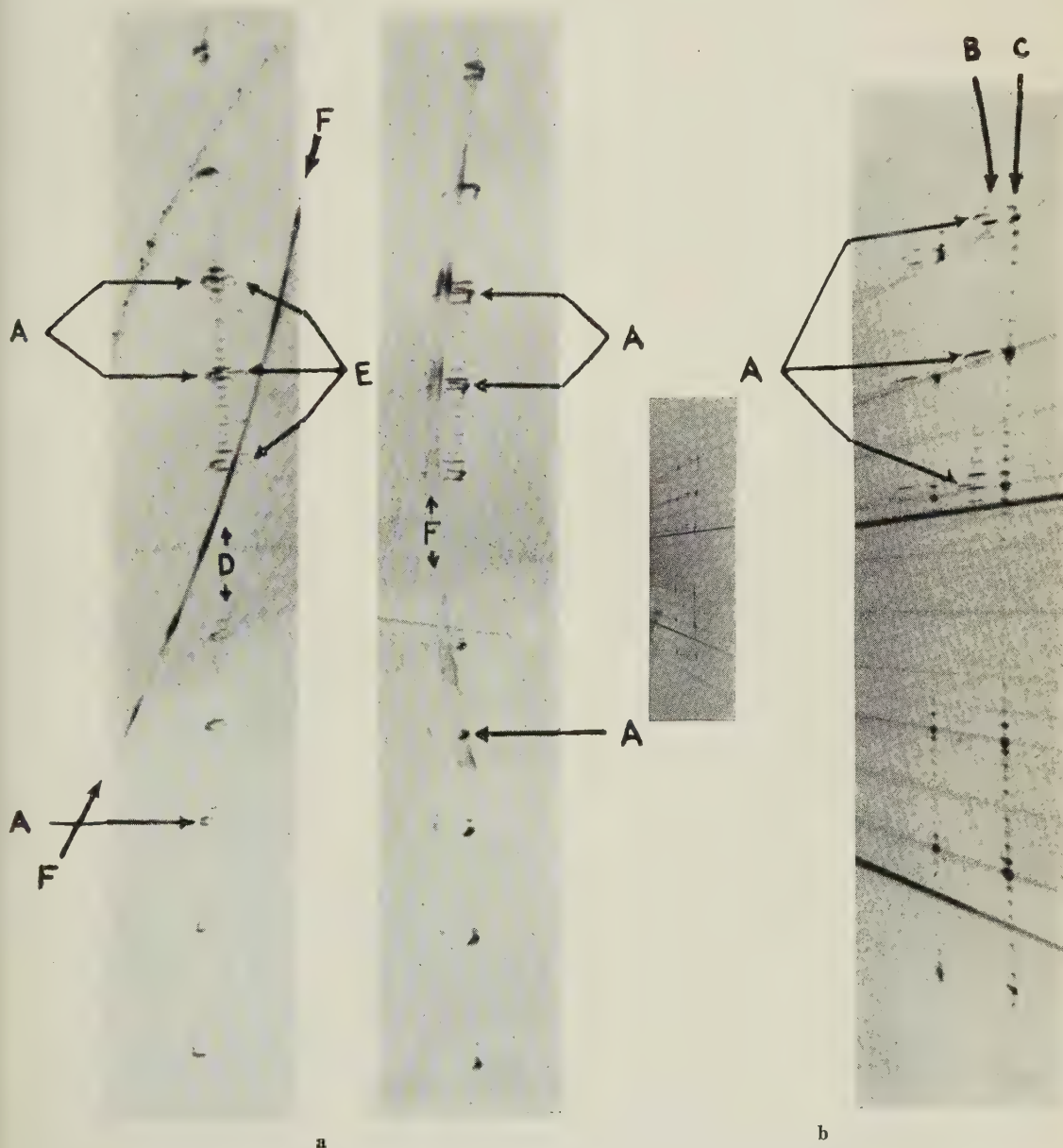


Fig. 1-a and -b. Oscillation photographs of SiC specimen containing the domains of 174-layer period. The left of **b** is the original of the right. The reflections indicated by **A** show 6-layer period, those **B**, **C**, **D** and **E** show 174-layer period, and **F** diffuse scattering.

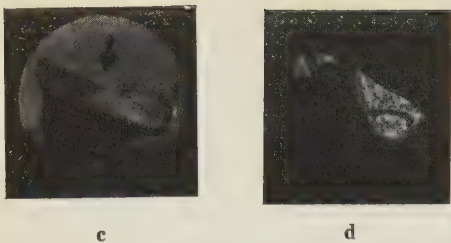


Fig. 1-**c** and -**d**. Micrographic photographs of the specimen ($\times 10$). The surface indicated by arrow in **c** is shown in **d**, on which many domains of 174-layer period exist.

§ 4. Determination of Structure

It is noted in Fig. 1-**a** and -**b** that the reflections due to 174-layer structure are strong in the vicinity of those due to six-layer period, and that relative intensity of them resembles that of ordinary six-layer structure

(CCH)₂. This suggests that the regular sequence of ordinary six-layer structure is dominant in the rhombohedral unit of 58-layers. The 58-layer period can contain, at maximum, nine sequence of six-layer structure. The sequences longer than seven, however, seem to be unlikely, since the corresponding minima of reflection would coincide with the observed intense reflections of $(10\bar{1}, 26)$, $(10\bar{1}, 32)$ and $(10\bar{1}, 83)$. Table I shows that the Laue functions arising from seven or more regular sequences of six-layer period have minima at every three or four periods of the reciprocal *c*-axis of 174-layer structure. $(10\bar{1}, 26)$, $(10\bar{1}, 32)$ of 174-layer structure occur at three reciprocal *c*-periods from $(10\bar{1}1)$ of six-layer period, and $(10\bar{1}, 62)$, $(10\bar{1}, 83)$ at four

Table I.

Number of sequence of 6-layer period	9	8	7	6	5	4	3
Angle between successive minima of Laue function	3.2	3.6	4.1	4.8	5.8	7.3	9.7

Angles between successive minima of Laue functions arising from various sequences of 6-layer period are shown by the unit of 174-layer reciprocal lattice period.

reciprocal *c*-periods from $(10\bar{1}2)$, $(10\bar{1}3)$ of six-layer period respectively. Other shorter sequences have also unfavourable minima, but they are always combined with certain sequence of layers to compose 58-layer period, and the unfavourable minima may be extinguished if we select an appropriate disposition of these separated sequences. Thus, the 58-layer period is considered to consist of three ranges, *P* and *Q*, having three to six regular sequences of six-layer structure, and the inter-range *R* having the layers of 58 minus those included in *P* and *Q* (Fig. 3).

The ranges *P* and *Q* occupy the main part of 58-layer period. The phase difference between the reflections from *P* and *Q* will appreciably affect the intensity distribution. For example, the relative disposition of *P* and *Q* should be such that $(10\bar{1}, 29)$ reflection, corresponding to 1/6 point of the reciprocal *c*-period of a Si-C layer, is far weaker than $(10\bar{1}, 116)$, 4/6 point. The consideration on this point will be described in detail in another paper⁷⁾.

For the stacking order in range *R*, we as-

sume 1) the continuation of either sequence of the range *P* or *Q*, Models 1 and 2 in Fig. 3, 2) those found in the structures reported for various periods corresponding to the number of layers, Models 5 and 8 in the figure, or those of no definite order, Model 7.

We should first refer two fundamental restrictions for the structure of silicon carbide that 1) any two successive layers do not occupy the same sites of A, B or C, and 2) both end layers of rhombohedral unit can be assumed to have the same sites of A, B or C as shown in Appendix.

Thus, 50 models for the new structure were constructed, and some of them are shown in Fig. 3. Here, 6*m* and 6*n* mean that the ranges *P* and *Q* consist of *m* and *n* sequences of six-layer structure, and *a*, *b*, *c* and *d* indicate the combinations of the possible numbers of *m* and *n*. In Model 1*a*, for example, *P* and *Q* have 4 and 5 sequences of six-layer structure respectively and are separated by *R* of 4 layers following the stacking order in *P*.

The 174-layer period contains three of each unit shown in Fig. 3, and the three units are

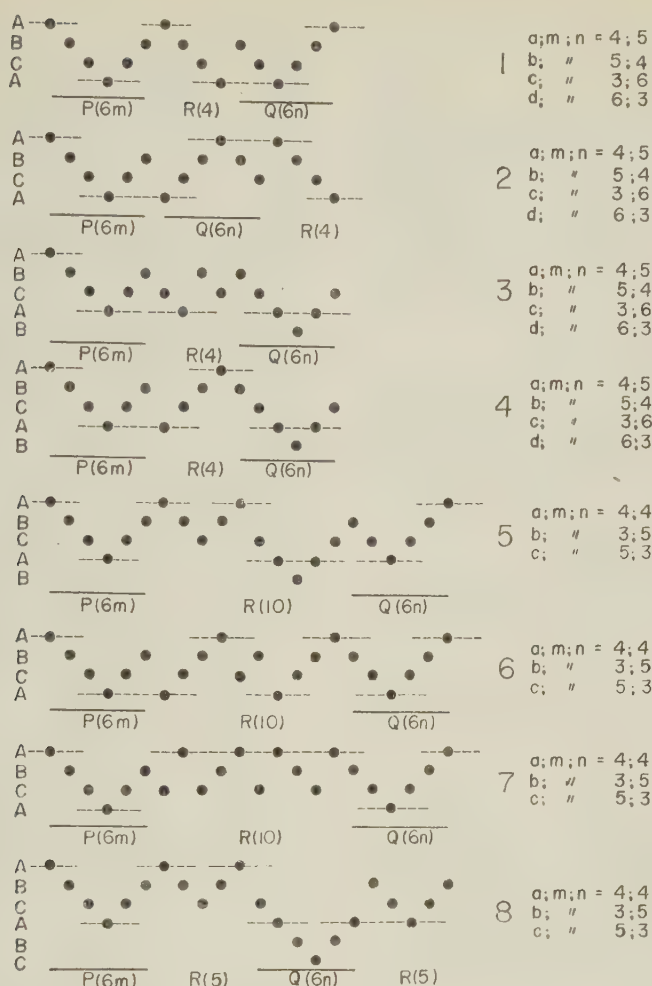


Fig. 3. Examples of possible model structures shown in (11 $\bar{2}$ 0) sections. m and n are the number of sequences of 6-layer structure in ranges P and Q . For each model, several combinations of possible m and n can be considered as indicated. R is the inter-range including the layers of the number of 58-6 ($m+n$). Those having opposite rhombohedral shift are distinguished from each other as Model 1a1 and 1a2, ABC from left to right being specified by 1, and the reversal by 2.

stacked with rhombohedral shift ABC or ACB. These two kinds of rhombohedral shifts produce two different structures from the same unit, for examples, 1a1 and 1a2; the shift ABC from left to right in Fig. 3 is specified by 1 and the reversal by 2.

The intensities for these models were calculated by the method given in a previous paper⁵⁾. The number of terms of the structure factor formula was so large that the error arising from round-off was negligible when four decimal figures were used.

Of these models, 1b2 which can be written as $\{C(CCH)_7C_3(CCH)_{11}\} \times 3$ by Wyckoff's nota-

tion gives the intensity of the best agreement with the observed intensity as shown in Fig. 4. Some other models, for examples, 6a1 represented as $\{C(CCH)_7C_9(CCH)_9\} \times 3$, and 1a1, represented as $\{C(CCH)_8C_3(CCH)_{10}\} \times 3$, show fairly good agreement with the observed as far as strong reflections are concerned (Table II), since they are different from 1b2 only in reversal of rhombohedral shift and the disposition of two successive layers at about middle of the rhombohedral unit. But, they reveal definite disagreements in the detailed intensity distributions; for 6a1, (10 $\bar{1}$,

50) reflection would be vanishingly weak while it has detectable intensity, and for 1a1, the reflections from (10 $\bar{1}$, 41) to (10 $\bar{1}$, 47) and from (10 $\bar{1}$, 71) to (10 $\bar{1}$, 77) etc. have intensity distributions quite different from the observed.

Thus, the new modification is concluded to have the structure represented as {C(CCH)₇C₃(CCH)₁₁} × 3.

spiral-terraces observed on SiC specimens and the *c*-periods of the structure, and Jagodzinski⁴⁾ proposed the layer-transposition mechanism caused by vibration entropy in order to construct the modifications found for silicon carbide and zinc blende. The structure of

Table II. Calculated intensities of (10 $\bar{1}l$) reflections for Models 1b2, 6a1 and 1a1.

Number of (10 $\bar{1}l$) reflections	Models		
	1b2	6a1	1a1
10 $\bar{1}$, 2	0	0	0
5	5	5	5
8	5	0	11
11	16	19	2
14	0	0	29
17	47	31	0
20	33	49	105
23	102	15	0
26	1191	1220	1318
29	157	131	131
32	1584	1545	1768
35	199	35	8
38	93	150	296
41	279	206	103
44	3	0	185
47	166	302	19
50	116	0	237
53	204	780	129
56	1645	549	1666
59	5583	3715	5598
62	226	870	184
65	89	72	183
68	140	290	17
71	4	4	147
74	163	112	6
77	52	35	187
80	171	63	15
83	741	668	857
86	1378	1325	1253
89	2772	2718	2871
92	178	30	92
95	111	38	186
98	97	25	28
101	16	12	74
104	52	105	16
107	21	79	45
110	20	170	9
113	35	131	35
116	6865	10075	6865
119	36	134	36
122	47	278	38
125	20	67	42
128	47	100	12
131	20	20	79
134	82	13	19
137	83	41	146
140	131	16	59
143	1994	1994	2064
146	784	870	711
149	343	309	402
152	58	0	12
155	13	9	54
158	28	12	0
161	3	3	18
164	5	13	5
167	5	5	3
170	2	8	2
173	0	0	0

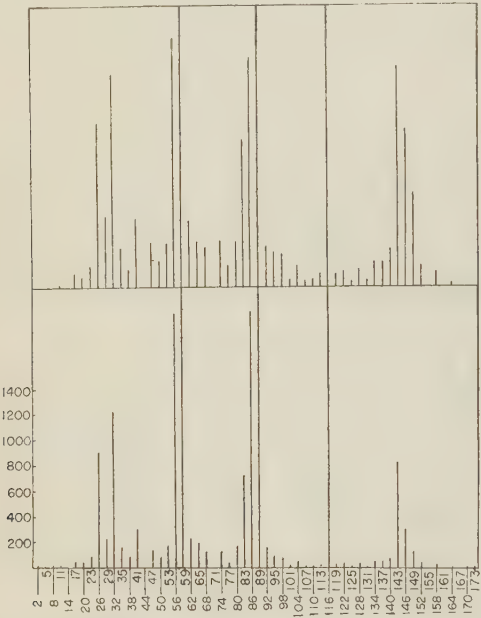


Fig. 4. Intensity distribution along (10 $\bar{1}l$) axis of (a) observed and (b) calculated.

§ 5. Discussion

The structure of new modification has the rhombohedral unit built from two ranges of ordinary six-layer structure separated by 4 layers. The two ranges are composed of, respectively, 5 and 4 sequences of six-layer structure orientating with each other mirror-symmetrically with respect to (0001) plane. 4 layers separating two ranges follow the stacking order of the range having 5 sequence. The 174-layer periods found for many domains, indicated in Fig. 1, show the same structure, and the production of it does not seem to be due to a trivial origin.

The growth mechanism for modification of such a long period is interesting, and several mechanisms have been proposed, e.g., the spiral growth mechanism was proposed by Frank¹⁾ and investigated by Verma^{8),9)} by the relations between the step-heights of the

the new modification may be constructed by either of these mechanisms. These mechanisms, however, can not explain the preferential occurrence of the observed stacking order.

Appendix

We shall prove here that both end layers of the rhombohedral unit can be assumed on the same sites of A, B or C. If we express the sites A, B and C by $\delta=0, 1$ and 2 , the site S_n^1 of n -th layer in the first rhombohedral unit can be represented as

$$S_n^1 = \delta; 0, 1 \text{ or } 2, \quad (1)$$

the suffix 1 indicating the first rhombodetral unit.

The site of n -th layer in the second rhombohedral unit, succeeding to the first, is

$$S_n^2 = \delta + 1 \quad (2)$$

for rhombohedral shift ABC, and the site of $(n-1)$ -th layer in the same unit is

$$S_{n-1}^2 = \delta \text{ or } S_{n-1}^2 = \delta + 2. \quad (3)$$

If $S_{n-1}^2 = \delta + 2$ occurs, the $(n-1)$ -th layer in the first unit should have the site

$$S_{n-1}^1 = \delta + 1, \quad (4)$$

and the relative shift between two successive layers is equal to

$$S_{n-1}^1 - S_n^1 = 1$$

by (1) and (4).

If the condition takes place for all n -th layers in the unit, the structure is not other

than rhombohedron of three layers, namely CCC. . . .

Thus, the rhombohedral structure, longer than three layers, have at least one period corresponding to rhombohedral unit having both end layers on the same sites by another condition of (3).

For reversed rhombohedral shift ACB shwon by $S_n^2 = \delta + 2$, the argument is quite similar.

Acknowledgements

The author wishes to thank Prof. Y. Sakisaka and Prof. S. Miyake for their kind remarks and encouragement and Prof. G. Honjo for his discussion over this work.

References

- 1) F. C. Frank: *Phil. Mag.* **42** (1951) 1014.
- 2) G. Honjo, S. Miyake and T. Tomita: *Acta Cryst.* **3** (1950) 396.
- 3) H. Jagodzinski: *Acta Cryst.* **2** (1949) 298.
- 4) H. Jagodzinski: *Neues Jb. Miner. Mh.* (1954) 209.
- 5) T. Tomita: *Sci. Rep. Saitama Univ. A*, **I**, **1** (1952) 45.
- 6) T. Tomita: *Sci. Rep. Saitama Univ. II*, **1** (1955) 49.
- 7) T. Tomita: *Sci. Rep. Saitama Univ. III*, **2** (1959) 115.
- 8) A. R. Verma: *Phil. Mag.* **42** (1951) 1005.
- 9) A. R. Verma: *Proc. Roy. Soc. A*, **228** (1955) 34.
- 10) R. W. G. Wyckoff: *Crystal Structure* (1948).

Electron Diffraction Study of Ice

By Kohji SHIMAOKA

*Tokyo Institute of Technology, Oh-okayama,
Tokyo, Japan*

(Received August 31, 1959)

Temperature ranges of formation of low temperature forms of ice and the hydrogen position in cubic and hexagonal forms were studied by electron diffraction. The ranges were found to vary according to the rate of condensation of water vapor and the discrepancies between the previous data for the ranges were attributed to the difference of the rate. Intensity of Debye-Scherrer patterns showed best agreement with Pauling's half-hydrogen model for cubic ice as well as for hexagonal ice. Difference radial distribution and two-dimensional difference Fourier analysis of cubic ice revealed also that Pauling's model is appropriate. From two-dimensional difference Fourier map of three different projections, O-H distance was found to be $0.96 \pm 0.03 \text{ \AA}$. By calculation, it was shown that a shift of electron cloud causes no appreciable shift of potential peak. An elliptical elongation of hydrogen peak perpendicular to O-H bond was observed, which can be attributed to a shift of H-O-H angle from the tetragonal angle as well as to anisotropic thermal vibration.

§ 1. Introduction

König¹⁾ has first found that ice crystallizes in a cubic structure when water vapor condenses at temperatures below -80°C . Oxygen atoms of cubic ice are arranged in a diamond type lattice of a lattice constant $a=6.36 \text{ \AA}$ with the same O-O distance, $2.75 \text{ \AA}$, as in the ordinary hexagonal ice. The arrangement of the oxygen atoms is similar to that of silicon atoms in cristobalite, while the arrangement in the usual hexagonal ice is similar to that in tridimite. Since König obtained the cubic ice as a product of the residual vapor in electron diffraction camera, there had been some concern as to the effect of impurities (Owston and Lonsdale²⁾). Recently, however, Honjo et al.³⁾ and Blackman and Lisgarten⁴⁾, by electron diffraction, and Shallcross and Carpenter⁵⁾, by X-ray diffraction, confirmed the existence of cubic form by condensing water vapor from prepared sources. Calculating electrostatic binding energy, Bjerrum⁶⁾ once concluded that the cubic form, if exist, is less stable at lower temperature. It was shown by Pitzer and Polissar⁷⁾, however, that this conclusion is largely negated when additional interactions were taken into account. Thus, now there is no doubt about the existence of cubic ice. But, concerning the temperature range of its

formation, the results of various authors do not coincide with each other.

An important problem about ice crystal is the position of hydrogen atoms, which can hardly be determined by X-ray diffraction. Pauling⁸⁾, Barnes⁹⁾, Bernal and Fowler¹⁰⁾ and Owston¹¹⁾ proposed various models for hexagonal ice. Pauling assumed a hydrogen atom statistically distributed on two positions on each O-O bond with an O-H distance of about $1.0 \text{ \AA}$, Barnes assumed a hydrogen atom at the center of each O-O bond and the last three authors assumed definite hydrogen position on each O-O bond with a O-H distance of about $1.0 \text{ \AA}$.

The hydrogen position in hexagonal ice was studied by neutron diffraction¹²⁾ and Peterson and Levy have recently showed, using single crystal of heavy ice, that Pauling's model is appropriate for hexagonal ice.

The scattering cross section of hydrogen atoms relative to those of heavier atoms is larger for electron than for X-rays (Laschkarew and Usyskin¹³⁾). Taking advantage of this fact, hydrogen atoms in some crystals were determined successfully by electron diffraction method (cf. Weinstein¹⁴⁾; Cowley¹⁵⁾). In previous communications some results of the electron diffraction studies of formation (Honjo et al.³⁾) and hydrogen position of cubic ice

(Honjo and Shimaoka¹⁶⁾) have been reported. In this paper the details will be described together with some additional results.

§ 2. Experimentals

1) General method

Experiments were carried out using the low temperature specimen method which had been reported previously in detail³⁾. Special precautions were paid to prevent the contamination of specimen by residual vapors. For this purpose, the apparatus was pre-evacuated up to about 2×10^{-5} mmHg and so, when the reservoir of refrigerant attached to the specimen holder was filled with liquid nitrogen, the vacuum of the specimen chamber reached to as high as 1×10^{-6} mmHg. Using a special shield, the specimen was exposed to residual vapors in the main volume of the apparatus only for short time when the diffraction pattern was observed. Thus, the deposit from residual vapor was reduced to a very small amount, presumably not more than a few Å in thickness.

2) The crystal formation

A polycrystalline specimen of ice was formed by condensing water vapor on substrates at various temperatures ranging from that of liquid nitrogen to above -60°C . For the specimen base, use is made of thin collodion film for transmission method and a natural surface of silicon carbide single crystal for reflection method. The latter method was mainly used in the study of the crystal formation, since the specimen of this method was of better thermal contact with refrigerant, so that the temperature of specimen is much less influenced by the irradiation of the electron beam than on thin collodion film.

The water vapor was supplied from a prepared source, a small piece of silica gel which had absorbed a suitable amount of water vapor. The vapor was lead into the specimen chamber through a cock and was ejected onto the substrates from a movable jet. The rate of condensation of water vapor was varied in a wide range by varying the amount of absorbed vapor and the position of the jet. Thus, the slowest rate of deposition was one or two order lower than that in the experiment of Blackman and Lisgarten.

3) The intensity measurement

As will be seen in the following section the

cubic ice formed at -150°C produced Debye ring patterns of no trace of hexagonal ice and no preferred orientation. Thus, the relative values of structure amplitude, $|F|$, were determined from the intensity of ring by the relation

$$I \sim p d^2 |F|^2,$$

where p is multiplicity and d is spacings.

The intensity measurement was carried out by the photometry of Debye patterns, taken at -195°C , -160°C and -120°C using s^1 -sector camera (Takagi¹⁷⁾). The relative photographic density was transformed to the relative intensity by Karle and Karle's method¹⁸⁾.

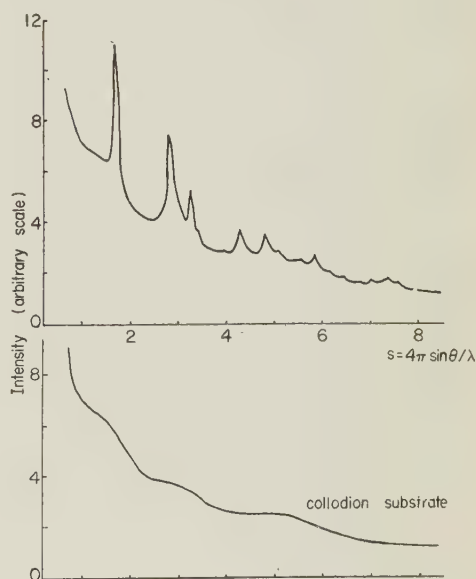


Fig. 1. The intensity curve of cubic ice and the collodion substrate.

Fig. 1 is an intensity curve of cubic ice on collodion substrate photographed at -195°C . The contribution of collodion base to this curve subtracted by comparing with an intensity curve of the halo pattern due to collodion film alone taken at the same temperature; since first halo is almost separated from the inner-most (111) reflection of cubic ice, the subtraction could be performed without serious difficulties. The half breadth of the coherent peaks was almost the same for all rings, and the relative intensity was obtained by measuring the peak height. From the breadth, the crystal size was estimated to be 80 Å using Scherrer's formula. The intensities of weak reflections of high orders were esti-

mated also by the visual method. The first column in Table I shows the percentage intensities of Debye rings due to cubic ice relative to that of (220) ring. The statistical deviation of the intensity data of 10 independent measurements were less than 15% in

average.

The temperature factor was determined using the above mentioned intensity data at three temperatures, assuming that the thermal vibration of atom was spherically symmetric. Thus, the Debye temperature θ was found to be $200 \pm 12^\circ\text{K}$, which nearly coincides with calorimetric value for hexagonal ice, 195°K (Owston¹⁹).

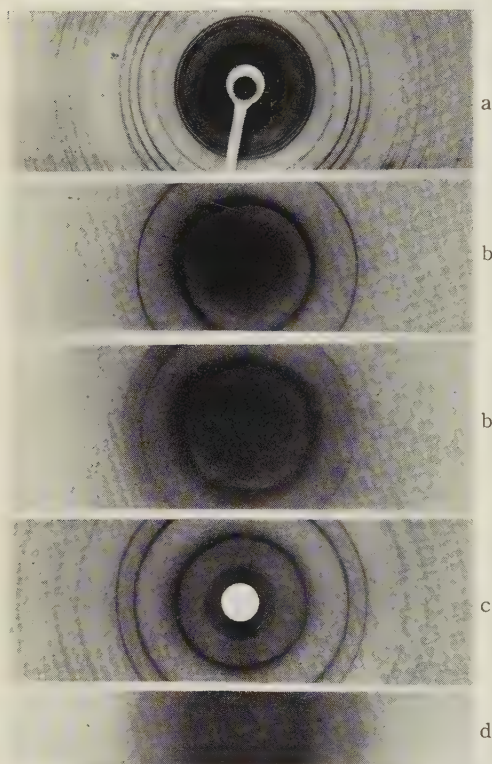


Fig. 2. Transmission electron diffraction patterns of ice formed on thin collodion films at temperatures a) -70°C , b) and b') -100°C , c) -150°C and d) -195°C .

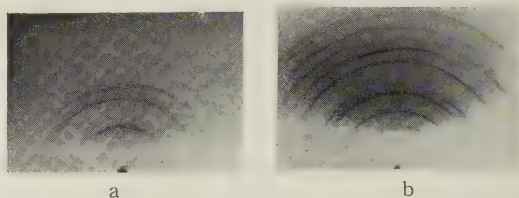


Fig. 4. Reflection electron diffraction patterns of ice formed on silicon carbide substrate at 100°C . a) is due to the initial deposit and b) is due to the deposit condensed rapidly on a).

§ 3. Study of the Crystal Formation

Typical electron diffraction patterns due to ice observed by the transmission method with normal incidence of electrons to the supporting film were reproduced in Fig. 2-a), b), c) and d). The characteristic features of the patterns are depicted schematically in Fig. 3. The patterns a) and c) correspond apparently to hexagonal and cubic ice, respectively, with the indices indicated in the figure. Almost all rings in the pattern b) can be indexed by the cubic lattice, but there are some strong additional rings corresponding to the basal reflections of hexagonal lattice such as (10, 0) and (12, 0). Since many rings of the basal reflections coincide with those of cubic lattice, the diffraction pattern can be considered to be due to the texture of the specimen composed of cubic ice of no preferred orientation and hexagonal ice of preferred orientation having basal plane parallel to the plane of substrate. In fact, non-basal hexagonal reflections did appear when the specimen film was inclined to the incident electron beam, as shown in Fig. 2-b'). Fig. 2-d) is a typical halo pattern.

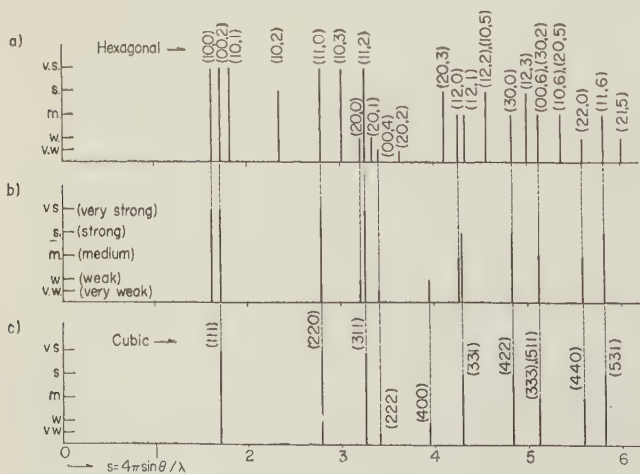


Fig. 3. Schematic features of three typical patterns Fig. 2-a), b) and c).

Above four types of diffraction patterns were obtained from the specimens of ice formed in the temperature ranges a) above -80°C , b)

from -80°C to -120°C , c) from -120°C to -150°C and d) from -150°C to -195°C , respectively. The intensity ratio between cubic and hexagonal rings from the specimen formed in the range b) varied according to the temperature of formation and the rate of deposition, the intensity of cubic rings increasing at the cost of that of hexagonal rings with decreasing temperature and decreasing rate of deposition. There was no indication for preferred orientation of cubic ice prepared in the range c).

Results of reflection experiments were similar to those of transmission experiments. It was noted, however, that at the initial stage of formation only cubic form was formed even above -120°C . When the rate of condensation was high, the ice formed on the initial layer was hexagonal having preferred orientation, (00, 1) paralleled to the

substrate surface, while, when the rate is slow, cubic ice continued to be formed. Fig. 4-a) and b) shows the reflection pattern obtained from the ice formed at -100°C ; a) shows the cubic pattern from the initial layer and b) shows the hexagonal pattern from the deposit on the former.

As for the transformation between various forms of ice, the following observations should be mentioned. When hexagonal ice was held at temperatures in the range from -100°C to -195°C , no change was observed on the pattern for a few hours, showing that transformation from hexagonal to cubic hardly occurs at low temperatures. In spite of the fact that the vapor pressure of ice exceeds 1×10^{-6} mmHg at about -100°C , ice layers survive on substrate above this temperature and electron diffraction pattern was observed sometimes for several minutes even at -65°C .

Table I. Observed and calculated intensities of cubic ice relative to that of (220) Debye ring put equal to 100.

<i>hkl</i>	<i>J</i> _{obs}	<i>I</i> _{obs}	<i>I</i> _c ⁰	<i>I</i> _P	<i>I</i> _B	<i>I</i> _z
111	257	235	145.9	222.5	238.0	216.1
200	—	—	0	0	0	0
220	100	100	100	100	100	100
311	38.5	40.8	58.4	35.4	32.4	37.5
222	1.6	1.7	0	2.63	5.07	3.14
400	5.5	5.9	15.0	7.51	5.70	7.78
331	19.5	24.2	21.7	26.8	32.6	27.3
420	—	—	0	0	0	0.65
422	13.9	19.0	25.6	20.5	24.4	20.4
333;511	4.9	7.0	13.2	6.96	7.30	7.16
440	3.5	5.6	6.54	8.00	10.9	8.65
531	7.4	12.5	10.5	9.12	14.9	9.30
442;600	0.0 ₈	0.1	0	0.23	0	—
620	1.1	2.1	7.67	5.10	7.30	—
533	0.9 ₆	1.8	3.18	3.20	1.78	—
622	—	—	0	0.02	0.53	almost equal to <i>I</i> _P —→
444	0.6	1.3	1.59	1.13	0.68	
551;711	2.0	4.6	3.93	4.23	5.61	
640	—	—	0	0	0	
642	3.4	8.6	6.07	6.11	5.78	
553;731	1.1	3.0	3.93	2.81	2.26	
800	0.1	0.2	0.47	0.38	0.80	
733	0.4	1.1	0.92	1.20	1.30	
644;820	—	—	0	0	—	
660;822	0.7	2.6	2.34	2.47	0.18	
555;751	0.5	1.8	1.50	1.50	0.90	
662	—	—	0	0	0.12	
840	0.3	1.2	1.09	1.00	0.52	
753;911	0.3	1.3	1.50	1.17	2.11	
842	—	—	0	0.08	0	
664	0.1	0.6	0.84	0.47	0.79	
931	0.2	0.8	0.77	0.85	0.45	
844	0.1	0.5	0.64	0.55	1.06	
771;755;933	0.1	0.7	0.91	0.66	1.44	
860;10,0,0	—	—	0	0	0	
862;10,2,0	0.2	1.4	1.55	1.47	1.56	

Similar phenomenon was reported by König and Blackman and Liscgarten. While these authors reported some indication of transformation from cubic to hexagonal at about -80°C , no definite such indication was recognized in the present experiment.

The ice formed at the temperature below -150°C , which shows halo pattern, was gradually transformed to the cubic ice when the temperature raised to above -150°C .

§ 4. Trial and Error Study of Hydrogen Position

1) Cubic ice

The observed relative intensity of cubic ice was tabulated in Table I, and compared with the intensities calculated for various models analogous to those proposed for hexagonal ice. In Fig. 5, the intensities were plotted on logarithmic scale, the calculated intensities being displaced vertically for clarity. Crosses represent the observed intensity I_{obs}^r , and plain circles, the intensity I_{obs}^r corrected for the temperature effect assuming $\Theta=203^{\circ}\text{K}$.

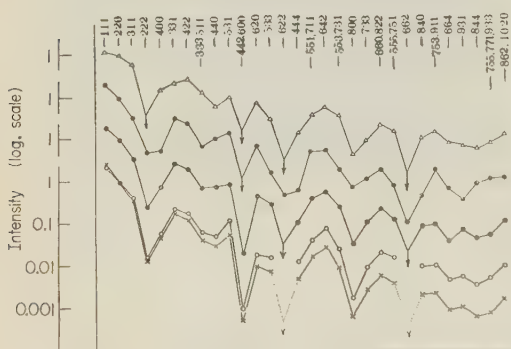


Fig. 5. Comparison of the relative intensities.

Triangles, black circles and dotted circles represent the calculated intensities, respectively, i) disregarding hydrogen scattering, $I_e^o \sim |F_e^o|^2$, ii) due to Pauling's half hydrogen model, $I_P \sim |F_P|^2$, and iii) due to Barnes' model, $I_B \sim |F_B|^2$. For the atom form factor of oxygen f^o and hydrogen f^H , the values given by Ibers²⁰ were used.

The primary extinction effect can be considered to be negligible in the present case; the maximum possible value of structure factor $F = \sum f_i$ is 3.34 volts at the angle of (111) reflection which corresponds to the value of the extinction coefficient $f(A)$ about 0.96 for

crystal thickness = $100 \text{ \AA}$ (Blackman²¹, Honjo and Kitamura²²).

In the lower order reflections, such as (111), (311), (222), (400), (422) and ((511), (333)) etc., the considerable differences were found between I_{obs} and I_e^o . This indicates that the contribution of hydrogen scattering were significant in the lower order reflections. The overall trend of the observed intensities can be fitted by Barnes' model as well as Pauling's model. The trend of the intensities (331), (440), (664) and (844), and the appearance of (222) and (442) and non-appearance of (622) and (662) reflections, however, are definitely more favorable for Pauling's model than for Barnes' model.

Using the scale factor given in the next section, reliability factor $R = \sum \|F_{\text{obs}} - F_{\text{cal}}\| / \sum \|F_{\text{obs}}\|$ was calculated and the values 8%, 19% and 20%, were obtained, respectively for F_P , F_B and F_e^o . Assuming Pauling's model the temperature factor was re-calculated by Wilson's method and a value $\Theta = 203^{\circ}\text{K}$ was obtained, which coincide well with the value determined from temperature variation of intensity.

Thus, the Pauling's model is most probable, though there are slight discrepancies in (440), (620) and (533) reflections. These discrepancies, $\delta = |I_{\text{obs}}^r - I_{\text{cal}}^r| / I_{\text{obs}}^r$, which exceeds 1.50, could not be eliminated by changing O-H bond length in a range from 0.90 to $1.05 \text{ \AA}$ as shown in Fig. 6.

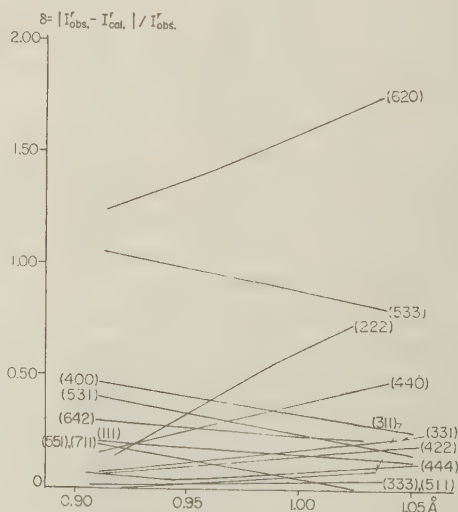


Fig. 6. The variation of the discrepancy parameter δ by changing O-H bond length in Pauling's model.

In the above consideration, only non-polar structure were considered. If we allow polarity, a structure model as shown in Fig. 7 can be conceived. This structure is not cubic but tetragonal belonging to $I4_1md$ (C_{4v}^{11}) with polar c -axis and gives Debye-Scherrer pattern of intensity quite similar to that due to Pauling's half hydrogen model as shown in the last column of Table I. Thus, as far as intensity data of Debye-Scherrer rings of lower orders are concerned, we can not rule out this structure. But, no indications for tetragonality of lattice parameter, namely, line splitting or unevenness of line breadth, were observed, and it seems very improvable, if not impossible, that such a tetragonal structure has an axial ratio exactly equal to unity.

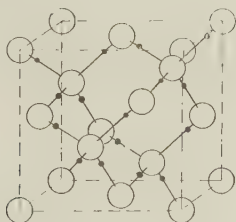


Fig. 7. Polar model for cubic ice.

2) Hexagonal ice

It was difficult to prepare specimens of hexagonal ice quite free from preferred orientation and admixture of cubic ice. Thus, no detailed study of its intensity was undertaken. But the following comment may be worth mentioning. Fig. 2-a) is due to specimen of comparatively weak preferred orientation. Fig. 8 shows the intensities calculated for Pauling's model (full lines) and for the super-lattice rings due to Owston's model (chain lines). This model containing eight- H_2O molecules was proposed taking into consideration the results of Bjerrum's calculation, and could not be eliminated by the early neutron diffraction data due to Wollan, Davidson and Shull¹²). When we compare Fig. 2-a) (Fig. 3-a)) with Fig. 8, it is noted that overall trend of the observed rings shows reasonable agreement with the calculated values for Pauling's model and that no trace of (00, 1), (10, 1) and (00, 3) reflections, which must be fairly strong for Owston's model, was observed, while their higher order reflections (00, 2) and (20, 2) could be certainly observed.

Thus, we can eliminate Owston's model. Similar conclusion can be drawn also for other super-lattice structures as proposed by Bernal and Fowler.

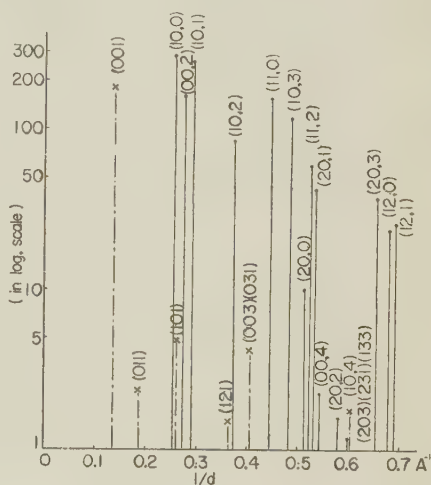


Fig. 8. Calculated intensities for Pauling's and Owston's models of hexagonal ice.

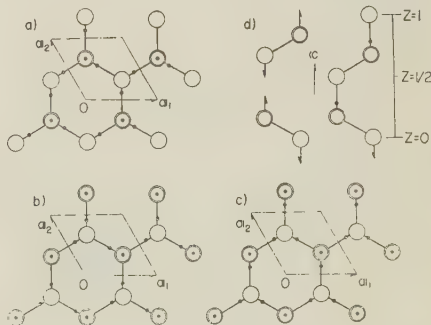


Fig. 9. Polar model for hexagonal ice. Black circles represent hydrogen atoms. Single and double plain circles represent oxygen atoms as shown in d). When a) be A-plane ($z=0$), b) or c) are possible for B-plane ($z=1/2$).

As in the case of cubic ice, we can construct a simple polar structure as shown in Fig. 9, which gives Debye-Scherrer pattern of intensity quite similar to that due to Pauling's model. Campbell²³) and Rossmann²⁴) have once reported the piezo- and pyro-electricities of hexagonal ice, but this was negated by latter experiments.

§ 5. Fourier Analysis

The hydrogen positions in cubic ice were studied by Fourier method: the difference radial distribution, two dimensional Fourier

map of potential distribution were synthesized from the observed data.

Wilson's statistical method to put the observed relative intensities on absolute scale is not favorable in the circumstance of the present case, that the crystal have high symmetry and the intensity of higher order reflections can hardly be measured with high accuracy. Thus, the observed intensities was put on the absolute scale in the following way. The potential distribution in the crystal can be given by

$$\varphi_{\text{obs}}(r) = V^o + V^H + \varepsilon \sum F_{\text{obs}}^r(s) \exp[i(s \cdot r)],$$

where V^o , V^H are mean inner potential of the crystal due to oxygen atoms and hydrogen atoms, respectively, ε is the scaling factor to be determined and s is the scattering vector of magnitude $s = |s| = 4\pi \sin \theta / \lambda$. The peak height of oxygen atoms in this distribution should be equal to the peak height in the potential distribution of oxygen frame work calculated by

$$\varphi_o^o = V^o + \sum F_o^o(s) \exp[i(s \cdot r)].$$

Therefore,

$$\begin{aligned} \varepsilon = & [\sum F_o^o(s) \exp[i(s \cdot r)] \\ & - V^H] / [\sum F_{\text{obs}}^r(s) \exp[i(s \cdot r)]] . \end{aligned}$$

V^H was calculated to be 1.04 volts assuming neutral hydrogen.

1) Radial distribution function

The difference radial distribution function

$$\begin{aligned} r^2 \Delta D(r) - r^2 D(r) - r^2 D_o^o(r) \\ = r^2 \int [(\varphi^o(r_1) \varphi^H(r_2) + \varphi^o(r_2) \varphi^H(r_1)) \\ + \varphi^H(r_1) \varphi^H(r_2)] dr_1 dr_2 \\ = r \sum_i s_i [I_{\text{obs}}(s_i) - I_o^o(s_i)] \sin(s_i r) \end{aligned}$$

was calculated from the observed intensity I_{obs} and the calculated intensity I_o^o . Here $\varphi^o(r)$ and $\varphi^H(r)$ represent the potential distribution due to oxygen atoms and hydrogen atoms, respectively, and the summation is taken over discrete numbers of Debye rings, s_i representing their s -values and $I_{\text{obs}}(s_i)$ and $I_o^o(s_i)$ the intensity of the i -th ring including the multiplicity. The zero-th term of this summation is given by $r^2[2V^oV^H + (V^H)^2]$. Actually the summation was taken upto $s=11$, and the result was shown in Fig. 10. This distribution function should consist of O-H and H-H peaks and not of O-O peaks which correspond to

$$r^2 D_o^o(r) = r^2 \int \varphi^o(r_1) \varphi^o(r_2) dr_1 dr_2 .$$

Though the H-H peaks can hardly be recognized in Fig. 10, O-H peaks are clearly found at about $r=1.0$ Å, well corresponding to Pauling's model. No peak is found at $r=1.38$ Å, corresponding to O-H distance in Barnes' model.

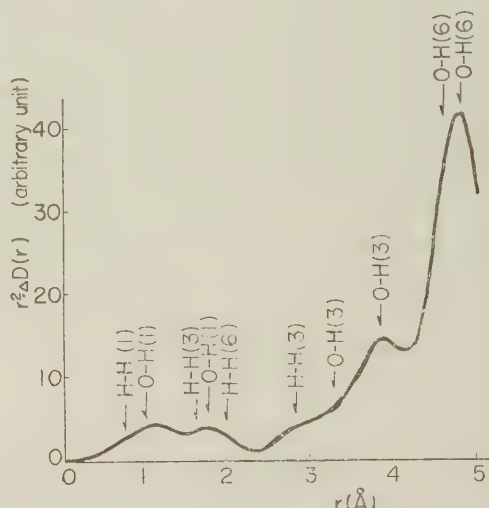


Fig. 10. Difference radial distribution curve.

2) Two dimensional Fourier synthesis

For the synthesis of the Fourier maps three premises had to be used. One is the assumption of the existence of the center of symmetry at the mid-point of O-O bond. The other premise is due to the circumstance that reflections having different indices, e.g. (660) and (820), overlap on the same Debye ring. In the present calculation, the intensities of such composite Debye rings were divided into their components with the ratio determined by Pauling's model. Fortunately, the intensities of such composite Debye rings were so weak that the results were not sensitively influenced by the ratio of the division. Divisions in other ratio such as in a ratio of the calculated intensities disregarding hydrogen scattering and in the ratio of multiplicities of reflections, gave nearly identical results. The sign of the structure factor $F(hkl)$ was determined according to that of $|F^o(hkl)|$, since it can naturally be considered that $|F^o(hkl)| > |F^H(hkl)|$. For reflections of $F_o^o=0$, the sign expected from Pauling's model was used; of these reflections, (222) was the only one used for the synthesis, and the sign is

independent of the position of hydrogen atoms so far as they are on O-O bond.

Two dimensional potential Fourier maps projected on (001), (110) and (111) plane were calculated by Beevers and Lipson's strip, the summation being terminated at (10, 2, 0), ((993), (755), (771)) and (862) reflections for the three projections, respectively, all corresponding to $s \approx 11$. Fig. 11 shows the potential Fourier map of the (001) projection calculated by using the structure amplitudes given by the square root of the observed intensities, J_{obs} , without correction of thermal effect. Two peaks at (0, 0), ($a/4, a/4$) are surely the potential peaks of oxygen atoms. In this map containing thermal vibration of atoms, the resolution is so poor that the indication of hydrogen atoms are only



Fig. 11. Potential Fourier map of (001) projection. The contour heights are shown in arbitrary scale.

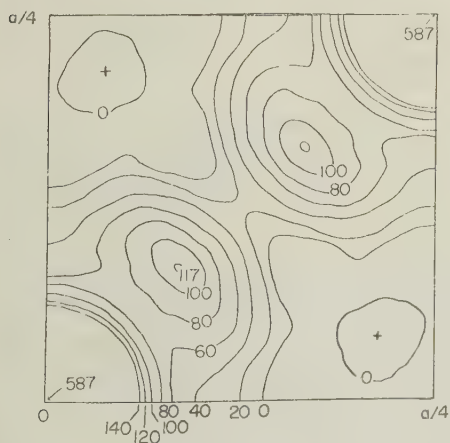


Fig. 12. Potential Fourier map of (001) projection corrected for the thermal effect. The unit of the contour scale is 0.37 volt·Å.

recognized as bulges of oxygen peaks along O-O bond. Fig. 12 shows the potential Fourier map of the same projection obtained from temperature corrected data assuming the Debye temperature $\theta = 203^\circ\text{K}$. The figures attached to contour lines represent the potential value in 0.37 volt·Å unit. The mean inner potential was calculated to be 3.70 volts by Tull's method²⁶⁾, assuming neutral oxygen and hydrogen atoms, of which $V^o = 2.64$ volts is due to oxygen atoms and the rest $V^H = 1.06$ volts to hydrogen atoms. For oxygen peaks at (0, 0) and ($a/4, a/4$), the contour lines above 140 units, or 52 volt·Å, were omitted. In this map, the termination effect is considerable as revealed by comparing it with the two dimensional potential Fourier map of the oxygen frame work of the same projection, Fig. 13, constructed by synthesizing $F_o^o(hkl)$ with the same termination. The sections of

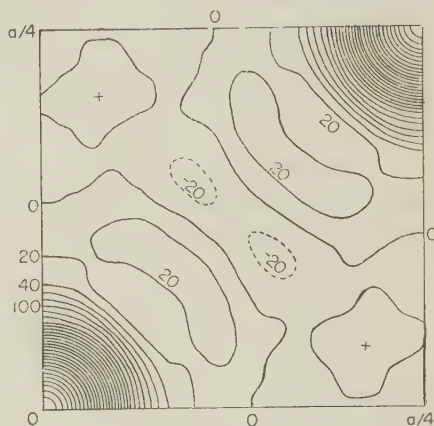


Fig. 13. Potential Fourier map of oxygen frame work projected on (001). The unit of the contour scale is 0.37 volt·Å.

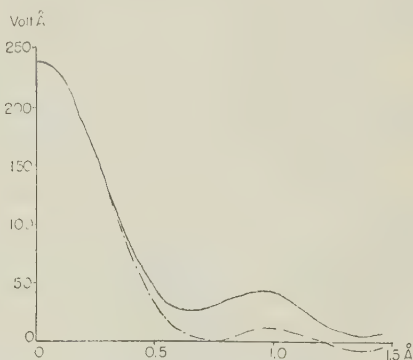


Fig. 14. Comparison of the sections along (110) in the maps of Fig. 12 (full line) and Fig. 13 (chain line).

Fig. 12 and Fig. 13 along O-O bond are compared in Fig. 14. We can see that the peaks marked by crosses in Fig. 12 are erroneous ones due to the termination effect, and that the two peaks on O-O bond are true ones though they are considerably affected by the same effect. Thus, the difference Fourier map, where the contribution of oxygen atoms, Fig. 13, was subtracted from Fig. 12, was constructed and shown in Fig. 15. In this map two peaks on O-O bond stand out in

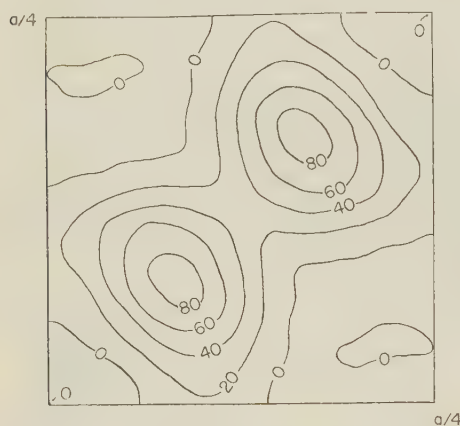


Fig. 15. Difference potential Fourier map projected on (001). The unit of the contour scale is $0.37 \text{ volt} \cdot \text{\AA}$.

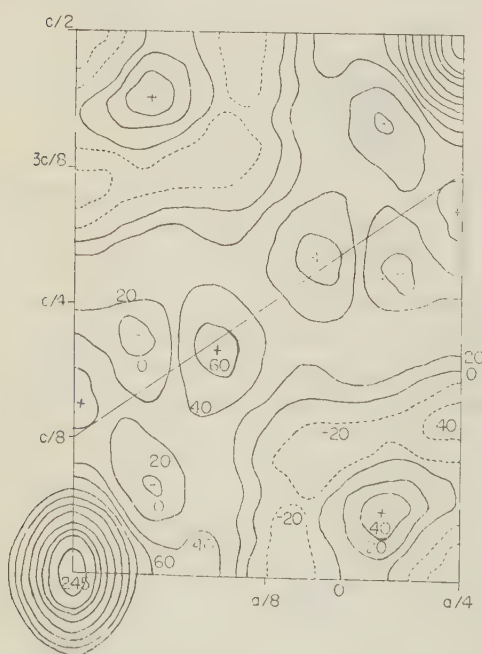


Fig. 16. Difference potential Fourier map projected on (110). The unit of the contour scale is $0.26 \text{ volt} \cdot \text{\AA}$.

relief against a smooth back ground. Their height is $30 \text{ volt} \cdot \text{\AA}$ (82 units) being $0.97 \text{\AA}$ distant from the oxygen atoms. It is noted that the shape of their contours is elliptically elongated perpendicular to O-O bond.

Fig. 16 reproduces the difference potential Fourier map projected on (110) and plotted with the unit of contour height equal to $0.26 \text{ volt} \cdot \text{\AA}$. In this projection oxygen atoms are at $(0, c/8)$. We find two separate peaks of a height about $20 \text{ volt} \cdot \text{\AA}$ (75 units) on the line connecting oxygen atoms and elongate peaks of height $65 \text{ volt} \cdot \text{\AA}$ (245 units) at $(0, 0)$ and $(a/4, c/2)$. The former two peaks are at a distance $0.98 \text{\AA}$ from the oxygen atom.

Fig. 17 reproduces the difference potential Fourier map projected on (111). In this projection oxygen atoms are at $(0, 0)$, $(a_r/2, b_r/6)$ and $(0, b_r/3)$. We find two elongate peaks of height $26 \text{ volt} \cdot \text{\AA}$ (41 units) at a distance $0.94 \text{\AA}$ from the oxygen on each line connecting these oxygen positions and circular peaks of height $48 \text{ volt} \cdot \text{\AA}$ (74 units) just upon the oxygen position.

Above mentioned peaks in the difference Fourier maps, Fig. 15, Fig. 16 and Fig. 17, can very reasonably explained by Pauling's half-hydrogen model: the three maps correspond to the areas in the dotted line of the Fig. 18-a), b) and c), respectively. The hydrogen peaks in (001) projection just correspond to two half-hydrogen atoms on the bond connecting two oxygen atoms marked by A and B in Fig. 18-d). In (110) projection, two peaks of $20 \text{ volt} \cdot \text{\AA}$ height correspond



Fig. 17. Difference potential Fourier map projected on (111). The unit of the contour scale is $0.64 \text{ volt} \cdot \text{\AA}$.

to the half-hydrogen atoms on AD-bond and the elongate peaks at (0, 0) and ($a/4$, $c/2$) correspond to 4-half-hydrogen atoms on AB and AC bonds unresolved on account of the foreshortening of the bonds. In (111) projection, the peak 48 volt·Å at ($a_r/2$, $b_r/6$) corresponds to 2-half-hydrogen atoms on AB projected edge on, and peaks of 26 volt·Å arranged hexagonally around it are half-hydrogen atoms on six O-O bonds, three around A-oxygen and three around B-oxygen. As shown in the next section a half-hydrogen is expected to give a peak of height about 25 volt·Å in two dimensional Fourier maps with the termination at $s=11 \text{ Å}^{-1}$. The observed peaks have reasonable height.

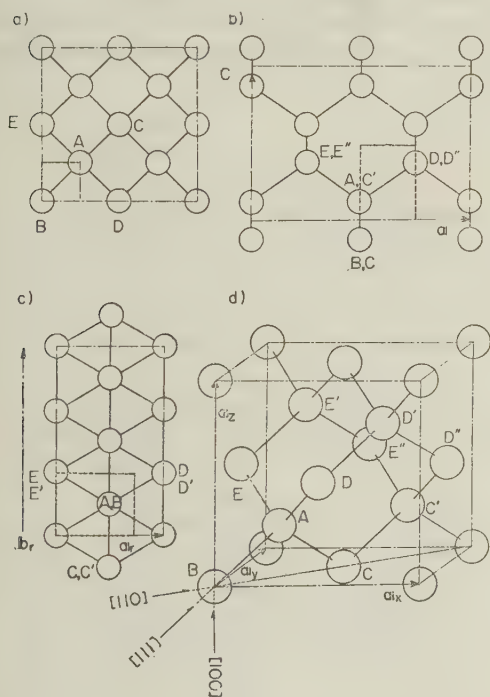


Fig. 18. Key diagrams for Fourier maps of cubic ice projected on a) (001), b) (110) and c) (111). d) represents the frame work of the cubic structure.

§ 6. Potential Distribution of Hydrogen Atom in Two Dimensional Fourier Map

The potential in an atom is the sum of the positive potential due to nucleus and the negative potential due to electron cloud. In crystal, the distribution of electrons must shift, more or less, from that in the isolated neutral atom. This may result in a deformation of contour lines of potential and a displacement

of potential peak from the position of nucleus. Following consideration gives a rough estimation of such effects and is useful for further discussion of the potential Fourier map obtained in the last section.

The two dimensional potential distribution in an isolated spherically symmetric atom, $\varphi(r)$, is given by Hankel inversion of the atomic scattering factor f_e for electrons:

$$\varphi(r) = (1/2\pi) \int_0^\infty f_e(s) J_0(sr) s ds \quad (1)$$

(Weinstein¹⁴), where J_0 is Bessel function of zero-th order. For hydrogen atoms,

$$f_e = (1 - f_x^H)/s^2,$$

where f_x^H is the atomic scattering factor for X-rays given by

$$f_x^H = \{4/(4 + a_B^2 s^2)\}^2,$$

a_B being Bohr's radius. Thus, the two-dimensional potential distribution φ^H of hydrogen atom, is the sum of the distribution $\varphi_n(r)$ due to nucleus (proton) and that, $\varphi_e(r)$, due to electron:

$$\varphi^H(r) = \varphi_n(r) + \varphi_e(r),$$

where

$$\varphi_n(r) = (1/2\pi) \int_0^\infty (1/s^2) J_0(sr) s ds, \quad (1a)$$

$$\varphi_e(r) = (1/2\pi) \int_0^\infty (-f_x^H/s^2) J_0(sr) s ds. \quad (1b)$$

Here, if we construct a function

$$\varphi^H(r, \Delta r) = \varphi_n(r) + \varphi_e(r + \Delta r),$$

this will give the potential distribution due to a "hydrogen atom", in which the center of electron distribution shifts a distance Δr from the position of proton. As the matter of fact, the integrals (1a), (1b) are both divergent and we can not calculate $\varphi^H(r, \Delta r)$. We can calculate, however, a similar potential distribution by the following way.

Consider a crystal composed only of hydrogen atoms. The two dimensional potential distribution of the crystal is given by

$$\varphi^H(x, y) = \varphi_n(x, y) + \varphi_e(x, y),$$

where

$$\begin{aligned} \varphi_n(x, y) &= (1/A) \{ F_n(000) \\ &\quad + 2 \sum F_n(hk0) \cos 2\pi(hx + ky) \}, \\ \varphi_e(x, y) &= (1/A) \{ F_e(000) \\ &\quad + 2 \sum F_e(hk0) \cos 2\pi(hx + ky) \}, \end{aligned}$$

provided that the crystal has a center of symmetry, φ_n and φ_e are the potential distribution

due to the nucleus and electron cloud, respectively. $F_n(hk0)$ and $F_e(hk0)$ are the crystal structure factors due to the nucleus and electron cloud, that is, they are given by attributing the scattering factors $1/s^2$ and $-f_x^u/s^2$, respectively, for each atomic position. The first terms of the series, $F_n(000)/A$ and $F_e(000)/A$, can not be known separately, but the sum of them, $\{F_n(000)+F_e(000)\}/A=F^H(000)/A$, can be calculated, since $F^H(000)/v$ is equal to V^H , where V^H is the mean inner potential of the crystal and v is the unit cell volume. The remainders

$$\varphi_n' = \varphi_n - F_n(000)/A$$

$$\varphi_e' = \varphi_e - F_e(000)/A$$

can be calculated with any desired approximation by summing up the series to corresponding terms. These φ_n' and φ_e' are the parts of potential distribution that determine the variation of potential relative to the levels determined by the mean inner potential. $\varphi_n'(r)$ and $\varphi_e'(r)$ were calculated for (001) projection of a hypothetical face centered cubic crystal of hydrogen of lattice constant $a=5.0$ Å. The mean inner potential of this crystal is calculated to be 0.8 volts by Tull's method. Series were terminated at $s=11$ Å⁻¹, the same as the Fourier series in the last section. The potential distribution along [110] axis are shown in Fig. 19-a) by full line. In this

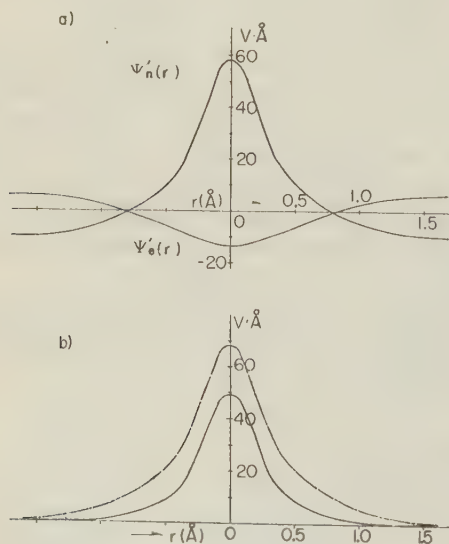


Fig. 19. Potential distribution of hydrogen atom. a) for proton and electron cloud. b) for hydrogen atom in normal (full line) and ionized (chain line) states.

direction, H-H distance is 3.5 Å. It is noted that $\varphi_n'(r)$ shows far steeper distribution than $\varphi_e'(r)$. This is, due to the fact that the former is the potential distribution due to point charge, while the latter is that due to electron cloud. For comparison, $\varphi_n'(r)$ and $\varphi_e'(r)$ were calculated with a termination at $s_{\max}=15$ Å⁻¹. $\varphi_n'(r)$ becomes higher and steeper with increasing $s_{\max}$, while $\varphi_e'(r)$ shows no difference for $s_{\max}$ larger than 10 Å⁻¹. The full line in Fig. 19-b) shows the sum of $\varphi_n'(r)$ and $\varphi_e'(r)$ for $s_{\max}=11$ Å⁻¹, plus $F^H(000)/A=a \cdot V^H=4.0$ volt·Å. This gives the potential distribution of the "neutral" hydrogen crystal. Fig. 20 shows the two-dimensional map of $\varphi_n'(r)+\varphi_e'(r+\Delta r)+F^H(000)/A$ for some values of Δr . These maps give the change of the two-dimensional potential distribution of a hydrogen atom in the crystal,

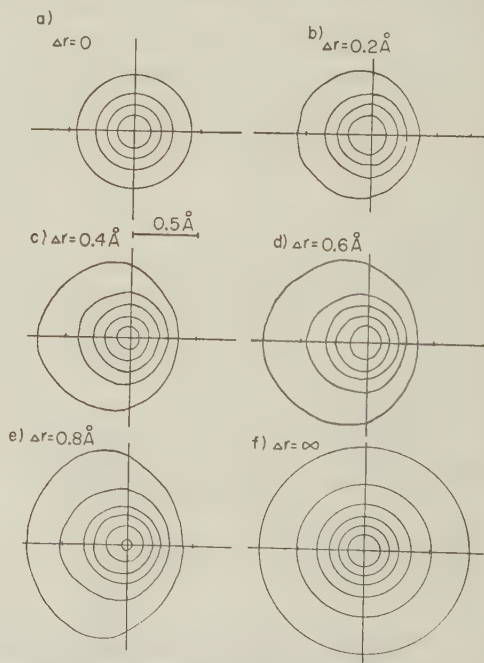


Fig. 20. Two dimensional distribution for hydrogen peak. Contours are drawn at an interval of 10 volt·Å. Contours of heights below 10 volt·Å are omitted.

when the center of electron cloud shift Δr from the position of nucleus, provided that the mean inner potential does not change with the shift. Fig. 20-a) corresponds to the neutral hydrogen atom, while Fig. 20-f) to the ionized state of the atom. By the shift Δr , the out-skirt of the potential distribution is distorted considerably, but there occurs no

appreciable change near the summit and the position of the peak nearly coincide with the position of nucleus. The shift of the peak position is at maximum 0.02 Å for $\Delta r=0.4$ Å.

It was assumed in the above consideration that electron cloud shifts without changing its spherical distribution. This assumption seems to be unreal and the distribution may be more or less elongated along the line of shift. According to the above result, however, such distortion also may affect only the out-skirt potential distribution and may not change the position of potential peak, especially in the direction of the elongation. The above calculation shows also that heights of 49 and 69 volt·Å are expected for the potential peak of neutral and completely ionized hydrogen atoms, respectively, in two-dimensional Fourier map with the termination at $S_{\max}=11$ Å⁻¹.

§ 7. Discussions

1) Crystal formation

In Table II summarizing the experimental data on the temperature ranges of formation of various forms of ice, the results of Blackman and Lisgarten and Shallcross and Carpenter are remarkably different from the

Table II. Summary of experimental results of crystal formation from water vapor on a base at low temperature.

Temperature ranges (°C)							
	-180	-160	-140	-120	-100	-80	-60
König	small crystals		cubic			hexagonal	
Honjo et al.	crystal growth poor		cubic			hexagonal	
Blackman & Lisgarten	amorphous or small crystal			cubic		hexagonal	
Shallcross & Carpenter	amorphous			cubic		hexagonal	
this paper	(halo pattern)			cubic		hexagonal	

others. It should be noted here the fact that Blackman and Lisgarten prepared ice crystal by condensing water vapor of higher vapor pressures, 10⁻¹~10⁻³ mmHg, while it was prepared from water vapor of pressures 10⁻⁴ mmHg in Honjo et al.'s experiment, and from residual water vapor of pressure, presumably, of the same order in König's experiment. The X-ray samples of Shallcross and Carpenter's experiment must have been also

prepared from water vapor of much higher vapor pressures. Therefore, the rate of condensation of water vapor must have been faster in Blackman and Lisgarten's and Shallcross and Carpenter's experiments than in the other electron diffraction studies. The result of present experiment shows that the temperature ranges vary considerably with the rate of condensation in such a way that the faster the condensation, the narrower the temperature range for cubic formation, and that the original data due to König, from -150°C to -80°C, is reasonable as the range for slow condensation. For fast condensation, it seems to be difficult to define the range, since the cubic sample prepared by rapid condensation is hardly free from hexagonal form. It is noted that the "cubic pattern" reproduced in Blackman and Lisgarten's paper shows the trace of (10, 3) hexagonal ring between (220) and (311) cubic rings.

Concerning the transformation from cubic to hexagonal form at high temperature, no definite evidence was found in the present experiment, which is not consistent with König's and Blackman and Lisgarten's reports. It is worth while to mention here the possibility that Blackman and Lisgarten and König had observed the pattern of hexagonal ice recondensed at high temperatures.

At present we can not say definitely whether the halo pattern, obtained at low temperatures, corresponds to amorphous or small crystals.

2) The position of hydrogen atoms

It was concluded that Pauling's half-hydrogen model is appropriate for cubic ice as well as for hexagonal ice. From the two dimensional Fourier maps shown in Section 5, the mean distance between oxygen and hydrogen peaks are found to be 0.96 ± 0.03 Å. As was seen in Section 6, this distance must be equal to the distance between nuclei of oxygen and hydrogen atom and should be compared with the neutron data for O-H distance in hexagonal ice, 1.01 Å, reported by Peterson and Levy. The present value is shorter than this value, though the difference exceeds only slightly the limit of accuracy of the psesent value. No reason can be conceived that the O-H bond length in cubic ice should be different from that in hexagonal ice. It is worth mentioning the fact that Kume and Kakiuchi²⁶⁾ recently have succeeded in deter-

mining the O-H bond length in hexagonal ice by the nuclear magnetic resonance and obtained a value $0.98 \pm 0.001 \text{ \AA}$ at -190°C , assuming that the hydrogen atom is on O-O bond.

3) The elliptical shape in the two dimensional potential distribution of hydrogen atom

It is noted in all two dimensional Fourier maps in Section 6, that hydrogen peaks show elliptical contours elongated perpendicular to O-H bond. For this fact following reasons may be conceived: i) termination effect of Fourier synthesis, ii) distortion of electron cloud, iii) shift of H-O-H bond angle from the tetragonal angle and iv) anisotropic thermal vibration. The first effect can be ruled out, since the difference Fourier map, constructed with the same termination, $s=11 \text{ \AA}^{-1}$ and composed of the structure factor calculated for Pauling's model, F_P , does not show elliptical but circular potential peaks of hydrogen atom. As was seen in Section 6, the second effect, if exist, can not distort so much the higher contours as observed. The third effect, suggested by Rundle²⁷⁾, is that the water molecule in ice crystal reserves the H-O-H bond angle, 104.5° , of free molecule and so arranged that one O-H branch of it is along O-O bond and the other O-H branch deviates

necessarily from the direction of O-O bond as shown in Fig. 21-a). When this deviation occur at random around each O-atom, the net effect appears on Fourier map as an elongation of hydrogen peak perpendicular to O-O bond. This effect as well as the anisotropic thermal effect can be taken into account by assuming that the hydrogen atom distributed with equal probability on a circle around O-O bond as shown in Fig. 21-b). The radius of circle u is estimated from Fourier map to be about $0.1 \text{ \AA}$. The atom form factor of hydrogen atom in such distribution, f_R^H , is given by

$$f_R^H = f^H \exp[-s^2 u^2 \sin^2 \phi / 4],$$

ϕ being the angle between the direction of O-O bond and the scattering vector $\mathbf{h}$. Using f_R^H , the structure factor F_R was calculated and compared with F_{obs} and F_P in Table III.

Table III. Comparison of the observed and calculated structure amplitudes.

hkl	F_{obs}	F_P	F_R	F_t
111	4.86	5.27	5.37	6.27
220	4.66	4.71	4.55	5.34
311	2.42	2.32	2.34	2.34
222	0.91	1.14	1.14	1.62
400	2.27	2.58	2.56	2.47
331	2.49	2.65	2.65	2.80
422	2.49	2.61	2.63	2.69
333	1.28	1.29	1.21	1.16
511	1.41	1.43	1.43	1.42
440	2.21	2.67	2.54	2.62
531	1.72	1.48	1.46	1.48
620	1.06	1.68	1.62	1.66
533	1.03	1.38	1.39	1.38
444	1.60	1.50	1.51	1.49
551	1.42	1.38	1.38	1.38
711	1.07	1.07	1.00	1.01
642	1.81	1.54	1.55	1.54
553	0.92	0.90	0.95	0.92
731	0.88	0.86	0.87	0.86

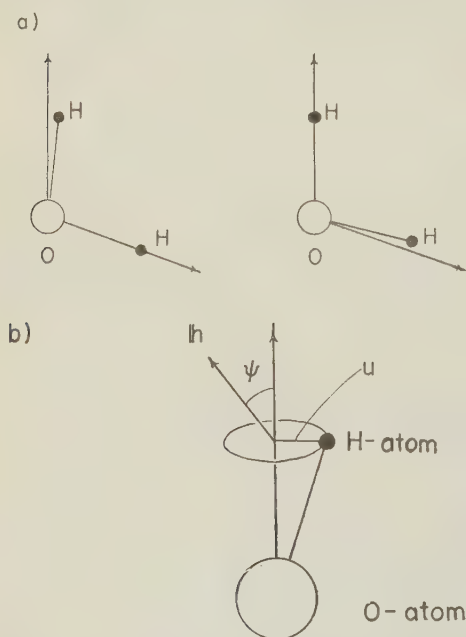


Fig. 21. Deviations of the hydrogen atom from O-O bond. Arrows represent O-O bond direction.

The agreement was slightly improved, resulting the reliability factor $R_R=7.7\%$, while that of simple Pauling's model $R_P=8.0\%$.

4) Ionization

With the accuracy of peak height in our Fourier maps, no definite conclusion can be drawn whether hydrogen atoms are ionized or not. But, it is noted that the calculated structure factors for completely ionized hydrogen atom gives worse agreement, $R_t=13\%$, than those for neutral hydrogen atom, $R=8.0\%$ (cf. Table III).

In conclusion, the author wishes to express

his sincere thanks to Prof. G. Honjo for his guidance throughout this work. The author's thanks are also due to Prof. S. Miyake for his valuable suggestion and encouragement and to Mr. N. Kitamura for his kind advice.

References

- 1) H. König: Nachr. Akad. Wiss. Göttingen, Math. Phys. K **1** (1942) Heft 1, 1; Z. Krist. **105** (1943) 273.
- 2) P. G. Owston and K. Lonsdale: J. Glaciol. **1** (1948) 118.
- 3) G. Honjo, N. Kitamura, K. Shimaoka and K. Mihama: J. Phys. Soc. Japan **11** (1956) 527.
- 4) M. Blackman and N. D. Lisgarten: Proc. Roy. Soc. A, **239** (1957) 93.
- 5) F. V. Shallcross and C. B. Carpenter: J. Chem. Phys. **26** (1957) 782.
- 6) N. Bjerrum: Dan. Mat. Fys. Medd. **27** (1951) no. 1; Science **115** (1952) 385.
- 7) K. S. Pitzer and J. Polissar: J. Phys. Chem. **60** (1956) 1140.
- 8) L. Pauling: J. Amer. Chem. Soc. **57** (1935) 2680.
- 9) W. H. Bernes: Proc. Roy. Soc. A, **125** (1929) 670.
- 10) J. D. Bernal and R. H. Fowler: J. Chem. Phys. **1** (1933) 515.
- 11) P. G. Owston: J. Chim. Phys. **50** (1953) (supplement) C-14.
- 12) E. O. Wollan, W. L. Davidson and C. G. Shull: Phys. Rev. **75** (1949) 1348. S. W. Peterson and H. A. Levy: Acta Cryst. **10** (1957) 70.
- 13) W. E. Laschkarew and I. D. Usyskin: J. Exp. Theor. Phys. U.S.S.R. **3** (1933) 510.
- 14) W. K. Weinstein: *Strukturная Elektronographia* (A. N. SSSR, Moscow, 1956).
- 15) J. M. Cowley: Acta Cryst. **6** (1953) 522.
- 16) G. Honjo and K. Shimaoka: Acta Cryst. **10** (1957) 710.
- 17) M. Takagi: Acta Cryst. **10** (1957) 708.
- 18) J. L. Karle and J. Karle: J. Chem. Phys. **17** (1949) 1052; J. Chem. Phys. **18** (1950) 963.
- 19) P. G. Owston: Quart. Rev. Chem. Soc. **5** (1951) 344.
- 20) J. A. Ibers: Acta Cryst. **11** (1958) 178.
- 21) M. Blackman: Proc. Roy. Soc. A, **173** (1939) 68.
- 22) G. Honjo and N. Kitamura: Acta Cryst. **10** (1957) 533.
- 23) E. S. Campbell: J. Chem. Phys. **20** (1952) 1413.
- 24) F. Rossmann: Experientia **6** (1950) 182.
- 25) V. F. D. Tull: Proc. Roy. Soc. A, **206** (1951) 232.
- 26) K. Kume and Y. Kakiuchi: to be published.
- 27) R. E. Rundle: J. Chem. Phys. **21** (1953) 1311.

Theory of Electron-Oscillations in Non-uniform Plasmas

By Masao SUMI

*Electrical Communication Laboratory
Musashino-shi, Tokyo, Japan*

(Received September 4, 1959)

For a system consisting of a medium-plasma and an externally injected beam with non-uniform density and temperature, electron-plasma oscillations are described on the basis of linear macroscopic equations. In the one-dimensional case the spatially growing plasma wave and the standing plasma wave are discussed. It is found that in the former a wave propagating towards decreasing density grows up higher than in the uniform case; in the latter the wave-length becomes shorter towards lower density and jumps of mode and frequency occur at a thickness of the layer greater than that in the uniform plasma. Towards increasing density the circumstances mentioned above are reversed. Finally a brief account is given on the two-dimensional case.

§ 1. Introduction

It has been known for many years that an electron beam, passing through a medium plasma, interacts closely with it and gives rise to plasma oscillations. When the plasma is uniform in space, various features of plasma waves have recently been investigated in a series of papers by the author.⁽¹⁾⁻⁽³⁾ However, when the plasma is non-uniform, the consequences obtained in the uniform case may be more or less modified. Besides a coupling between longitudinal and transversal waves will appear owing to gradients of density and temperature.

For non-uniform thermal plasmas in which no electron beam is present, electron-plasma oscillations have been treated in several papers.⁽⁴⁾⁻⁽⁸⁾ Among them radiations emitted from plasma oscillations owing to density and temperature gradients have also been discussed.⁽⁶⁾⁽⁸⁾

In most cases of gaseous discharge, there exist non-uniform regions in thermal plasmas, through which electron beams are running. Therefore it is of importance to clarify effects of non-uniformity on plasma waves excited in such a medium.

In the next section macroscopic equations for the system of thermal plasma and incident electron beam will be presented and linearized for oscillating components under suitable assumptions. The following two sections will deal with one-dimensional cases, in which plasma waves are independent of trans-

versal ones or radiations. In § 3 the case of spatially growing plasma waves will be examined where the interaction of the beam modulated at an incident boundary with the plasma causes the amplification of modulation. The behaviours of standing plasma waves will also be treated in § 4. The main purpose of these two sections will be to make apparent some modifications due to non-uniformity by comparing results obtained with those in uniform cases. In § 5, a brief consideration will be given in two-dimensional cases, where plasma waves will be coupled with radiation.

§ 2. Basic Formulations

To take into account effects of density and temperature gradients it is more convenient to treat plasmas macroscopically, since quantities such as density and temperature can be expressed explicitly in fundamental equations. The macroscopic or phenomenological theory of plasma has been developed by Kihara⁽⁹⁾ in general form. In a similar way as his, fundamental equations with respect to the j -th species, of which a plasma is composed, may be written as follows:

$$-\frac{\partial}{\partial t}(m_j n_j) + \nabla \cdot (m_j n_j \mathbf{v}_j) = 0, \quad (2.1)$$

$$\begin{aligned} -\frac{\partial}{\partial t}(m_j n_j \mathbf{v}_j) = & e_j n_j (\mathbf{E} + \mathbf{v}_j \times \mathbf{B}) - \nabla \cdot (\mathbf{P}_j \\ & + m_j n_j \mathbf{v}_j \mathbf{v}_j), \end{aligned} \quad (2.2)$$

$$\frac{\partial \theta_j}{\partial t} + \mathbf{v}_j \cdot \nabla \theta_j = -\frac{2}{f n_j} (\nabla \cdot \mathbf{q}_j + \mathbf{P}_j : \nabla \mathbf{v}_j). \quad (2.3)$$

The first is the equation of continuity where m_j , n_j and $\mathbf{v}_j$ are the particle mass, the number density and the mean velocity of the j -th species respectively. The second represents the equation of motion in which the electric charge of the partial-pressure tensor of this species are respectively denoted by e_j and $\mathbf{P}_j$. The resistance acting on this species is neglected, as we consider only a rarefied plasma with negligible friction. The gravitational force is also discarded. The third corresponds to the equation of thermal energy; $(f/1)\theta_j$ is the mean thermal energy per particle where f is the number of degrees of freedom of the particle and θ_j is connected with the temperature T_j in such a way as $\theta_j = \kappa T_j$, κ being the Boltzmann constant. $\mathbf{q}_j$ denotes the heat flux of the j -th species.

Here let us assume that the partial-pressure tensor is reduced to a scalar, which means that the viscous effect is ignored. Hence

$$\mathbf{P}_j = n_j \theta_j \mathbf{I},$$

where $\mathbf{I}$ is the unit tensor. In general the heat-flow term does not always vanish in the non-uniform plasma, but we shall neglect it as it would be justified for our study of rapidly varying processes such as plasma oscillations. Thus Eqs. (2.1) to (2.3) become

$$\frac{\partial n_j}{\partial t} + \nabla \cdot (n_j \mathbf{v}_j) = 0, \quad (2.4)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_j \cdot \nabla \right) \mathbf{v}_j = \frac{e_j}{m_j} (\mathbf{E} + \mathbf{v}_j \times \mathbf{B}) - \frac{1}{m_j n_j} \nabla (n_j \theta_j), \quad (2.5)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_j \cdot \nabla \right) \theta_j = - \frac{2}{f} \theta_j \nabla \cdot \mathbf{v}_j. \quad (2.6)$$

Together with these, the following Maxwell equations must be satisfied.

$$\nabla \times \mathbf{E} = - \frac{\partial \mathbf{B}}{\partial t}, \quad (2.7)$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \sum_j e_j n_j \mathbf{v}_j, \quad (2.8)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (2.9)$$

$$\nabla \cdot \mathbf{D} = \sum_j e_j n_j. \quad (2.10)$$

Here we assume $\mathbf{D} = \epsilon_0 \mathbf{E}$ and $\mathbf{B} = \mu_0 \mathbf{H}$.

Now we consider a system composed of a non-uniform plasma and an electron beam. Positive ions are supposed to constitute a continuous background almost neutralizing negative charges of electrons on the average. Accordingly one species in this system is electrons in the medium plasma and the other is those in the beam.

Hereafter we write the subscript j as p for the former species and as b for the latter and put $-e$ and m in place of e_j and m_j respectively. We first consider a stationary relation for the medium plasma. If there is a hydrostatic pressure gradient, we may suppose that the electron fluid will flow much more rapidly than the ions as is usually assumed. Thus a slight charge-separation will be induced and it will give rise to an electrostatic field $\mathbf{E}_0$, which, in turn, will restrain the electron flow, resulting an immediate equilibrium state. Therefore in this state $\mathbf{v}_{p0} = 0$ and Eq. (2.5) gives a relation of balance

$$e\mathbf{E} + \frac{1}{n_{p0}} \nabla (n_{p0} \theta_{p0}) = 0, \quad (2.11)$$

where the suffix 0 represents a stationary or equilibrium state. Then the number density of electrons n_{i0} is a little different from that of ions n_{i0} . Denoting its difference by δn_{p0} , the electrostatic field $\mathbf{E}_0$ satisfies

$$\nabla \cdot \mathbf{E}_0 = \frac{e}{\epsilon_0} (n_{i0} - n_{p0}) = - \frac{e}{\epsilon_0} \delta n_{p0}, \quad (2.12)$$

which gives, by Eq. (2.11),

$$\delta n_{p0} = \frac{\epsilon_0}{e^2} \nabla \cdot \left[\frac{\nabla (n_{p0} \theta_{p0})}{n_{p0}} \right].$$

It is easily shown that δn_{p0} is much smaller than n_{p0} , if n_{p0} and θ_{p0} are slowly varying functions of position. Thus a condition of quasi-neutrality of electric charge is fulfilled even in the presence of non-uniformity.

For the beam, we simply assume that all the electrons have the same velocity and hence the temperature of the beam vanishes, or $\theta_{b0} = 0$. Thus Eq. (2.4) becomes

$$\nabla \cdot (n_{b0} \mathbf{v}_{b0}) = (\mathbf{v}_{b0} \cdot \nabla) n_{b0} = 0. \quad (2.13)$$

Next we shall derive linearized equations of oscillating components for this system. For the medium plasma Eqs. (2.4)–(2.6) can be linearized as

$$\frac{\partial}{\partial t} \left(\frac{n_{p1}}{n_{p0}} \right) = - \nabla \cdot \mathbf{v}_{p1} - \mathbf{v}_{p1} \cdot \frac{\nabla n_{p0}}{n_{p0}}, \quad (2.14)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{v}_{p1} = & - \frac{e}{m} \mathbf{E} - \frac{\theta_{p0}}{m} \left[\nabla \left(\frac{n_{p1}}{n_{p0}} + \frac{\theta_{p1}}{\theta_{p0}} \right) \right. \\ & \left. + \frac{\theta_{p1}}{\theta_{p0}} \left(\frac{\nabla n_{p0}}{n_{p0}} + \frac{\nabla \theta_{p0}}{\theta_{p0}} \right) \right], \end{aligned} \quad (2.15)$$

$$\frac{\partial}{\partial t} \left(\frac{\theta_{p1}}{\theta_{p0}} \right) = -\frac{2}{f} \nabla \cdot \mathbf{v}_{p1} - \mathbf{v}_{p1} \cdot \frac{\nabla \theta_{p0}}{\theta_{p0}}, \quad (2.16)$$

where the subscript 1 represents the oscillating component. Now it is convenient to introduce a displacement vector $\mathbf{A}_p$ defined by

$$\mathbf{v}_{p1} = \frac{\partial}{\partial t} \mathbf{A}_p. \quad (2.17)$$

Then Eqs. (2.14) and (2.16) give

$$\frac{n_{p1}}{n_{p0}} = -\nabla \cdot \mathbf{A}_p - \mathbf{A}_p \cdot \frac{\nabla n_{p0}}{n_{p0}},$$

$$\frac{\theta_{p1}}{\theta_{p0}} = -\frac{2}{f} \nabla \cdot \mathbf{A}_p - \mathbf{A}_p \cdot \frac{\nabla \theta_{p0}}{\theta_{p0}}.$$

Inserting these into Eq. (2.25), we finally obtain

$$\begin{aligned} \frac{\partial^2 \mathbf{A}_p}{\partial t^2} = & -\frac{e}{m} \mathbf{E} + \frac{\gamma \theta_p}{m} \nabla \nabla \cdot \mathbf{A}_p + \frac{\theta_p}{m} \left[\frac{2}{f} \nabla \cdot \mathbf{A}_p \left(\frac{\nabla n_p}{n_p} \right. \right. \\ & + \left. \left. \frac{\nabla \theta_p}{\theta_p} \right) + \left(\frac{\nabla n_p}{n_p} + \frac{\nabla \theta_p}{\theta_p} \cdot \nabla \right) \mathbf{A}_p \right. \\ & + \left. \left(\frac{\nabla n_p}{n_p} + \frac{\nabla \theta_p}{\theta_p} \right) \times \nabla \times \mathbf{A}_p + \left(\mathbf{A}_p \cdot \nabla \right. \right. \\ & + \left. \left. \frac{\nabla \theta_p}{\theta_p} \right) \left(\frac{\nabla n_p}{\theta_p} + \frac{\nabla \theta_p}{\theta_p} \right) \right], \end{aligned} \quad (2.18)$$

where $\gamma = (2/f) + 1$ and the subscript 0 is suppressed. The last term on the right-hand side of this equation comes from gradients of density and temperature in the medium plasma.

For the electron beam we can put $\theta_{b1} = 0$, Eqs. (2.4) and (2.5) are now reduced to

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_{b0} \cdot \nabla \right) n_{b1} = -\nabla \cdot (n_{b0} \mathbf{v}_{b1}), \quad (2.19)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_{b0} \cdot \nabla \right) \mathbf{v}_{b1} = -\frac{e}{m} (\mathbf{E} + \mu_0 \mathbf{v}_{b0} \times \mathbf{H}). \quad (2.20)$$

Here we introduce a vector variable $\mathbf{A}_b$ such as

$$\mathbf{v}_{b1} = \left(\frac{\partial}{\partial t} + \mathbf{v}_{b0} \cdot \nabla \right) \mathbf{A}_b. \quad (2.21)$$

Inserting this into Eq. (2.19), we get

$$n_{b1} = -\nabla \cdot (n_{b0} \mathbf{A}_b). \quad (2.22)$$

Thus Eq. (2.20) gives, by the help of Eq. (2.7),

$$\frac{\partial}{\partial t} \left(\frac{\partial}{\partial t} + \mathbf{v}_{b0} \cdot \nabla \right)^2 \mathbf{A}_b = -\frac{e}{m} \left(\frac{\partial \mathbf{E}}{\partial t} - \mathbf{v}_{b0} \times \nabla \times \mathbf{E} \right) \quad (2.23)$$

Further, from Maxwell Equations we find for this system

$$\begin{aligned} \nabla \times \nabla \times \mathbf{E} + \epsilon_0 \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} - e \mu_0 \frac{\partial}{\partial t} (n_{p0} \mathbf{v}_{p1} + n_{b0} \mathbf{v}_{b1} \\ + n_{b1} \mathbf{v}_{b0}) = 0, \end{aligned}$$

which becomes, by inserting Eqs. (2.17), (2.21) and (2.22)

$$\begin{aligned} c^2 \nabla \times \nabla \times \mathbf{E} + \frac{\partial^2 \mathbf{E}}{\partial t^2} - \frac{e}{\epsilon_0} \left[n_{p0} \frac{\partial^2 \mathbf{A}_p}{\partial t^2} \right. \\ + n_{b0} \left(\frac{\partial}{\partial t} + \mathbf{v}_{b0} \cdot \nabla \right) \frac{\partial \mathbf{A}_b}{\partial t} - \mathbf{v}_{b0} \cdot \left(n_{b0} \frac{\partial \mathbf{A}_b}{\partial t} \right) \left. \right] \\ = 0. \end{aligned} \quad (2.24)$$

Thus Eqs. (2.18) (2.23) and (2.24) are the fundamental equations of this system for three variables $\mathbf{E}$, $\mathbf{A}_p$ and $\mathbf{A}_b$. It is, in general, very complicated to get, say, the equation of $\mathbf{E}$ alone by eliminating two other variables from these equations. Therefore we shall make further simplifications in later discussions.

Now we consider the one-dimensional case where all quantities are functions of z and t . Then we get the following equations of z -components from Eqs. (2.18), (2.23) and (2.24)

$$\left[\frac{\partial^2}{\partial t^2} - \frac{\gamma \theta_p}{m} \left(\frac{\partial}{\partial z} + D_z \right) \frac{\partial}{\partial z} - \frac{\theta_p}{m} \left\{ \frac{\partial}{\partial z} D_z + \frac{\partial}{\partial z} (\ln \theta_p) D_z \right\} \right] A_{pz} = -\frac{e}{m} E_z, \quad (2.25)$$

$$\left(\frac{\partial}{\partial t} + v_b \frac{\partial}{\partial z} \right)^2 A_{bz} = -\frac{e}{m} E_z, \quad (2.26)$$

$$E_z = \frac{e}{\epsilon_0} (n_p A_{pz} + n_b A_{bz}), \quad (2.27)$$

where $D_z = \partial(\ln n_p \theta_p)/\partial z$. They correspond to longitudinal oscillations. Similarly equations of both x and y components can be written separately and they represent transversal oscillations. The separability of components means that in the one-dimensional case there exists no coupling between longitudinal and transversal waves even in non-uniform plasmas. Details of longitudinal waves will be treated in the next section.

In the two-dimensional problem the longitudinal wave cannot be separated from the transversal one. This case will be discussed in a later section.

§ 3. Case of Spatially Growing Plasma Wave

In this section we first take a cold plasma, so that $\theta_p = 0$. Then Eq. (2.25) is simply reduced to

$$\frac{\partial^2}{\partial t^2} A_p = -\frac{e}{m} E. \quad (3.1)$$

Hence, combining this with Eqs. (2.26) and (2.27), we get for E the equation.

$$\left[\left(\frac{\partial}{\partial t} + v_b \frac{\partial}{\partial z} \right)^2 \left(\frac{\partial^2}{\partial t^2} + \omega_p^2 \right) + \omega_b^2 \frac{\partial^2}{\partial t^2} \right] E = 0,$$

where $\omega_p^2 = n_p e^2 / m \epsilon_0$, $\omega_b^2 = n_b e^2 / m \epsilon_0$ and the subscript z is omitted. Considering that n_p is a function of z , the above equation becomes

$$\begin{aligned} & \left[\left(\frac{\partial^2}{\partial t^2} + \omega_p^2 \right) \left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial z} \right)^2 + \omega_b^2 \frac{\partial^2}{\partial t^2} \right. \\ & \quad + 2v\omega_p^2 \frac{1}{n_p} \frac{dn_p}{dz} \left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial z} \right) \\ & \quad \left. + v^2 \omega_p^2 \frac{1}{n_p} \frac{d^2 n_p}{dz^2} \right] E = 0, \end{aligned} \quad (3.2)$$

where v_b is simply written as v .

Now we consider a spatially growing plasma wave. In the uniform plasma this case has been discussed in the previous paper.²⁾ Hence changes of wave-characteristics due to non-uniformity will be investigated here.

We suppose the beam modulating with a constant frequency ω at an incident boundary, so that the time variation of the oscillating field E may be put $\exp(-i\omega t)$. Thus Eq. (3.2) can be written as

$$\begin{aligned} & \left[\frac{\partial^2}{\partial z^2} - 2 \left(i \frac{\omega}{v} - \frac{\omega_p^2}{\omega_p^2 - \omega^2} \frac{n'}{n} \right) \frac{\partial}{\partial z} - \left\{ \frac{\omega^2}{v^2} \right. \right. \\ & \quad \left(1 + \frac{\omega_p^2}{\omega_p^2 - \omega^2} \right) + 2i \frac{\omega}{v} \cdot \frac{\omega_p^2}{(\omega_p^2 - \omega^2)} \frac{n'}{n} \\ & \quad \left. \left. - \frac{\omega_p^2}{\omega_p^2 - \omega^2} \frac{n''}{n} \right\} \right] E = 0, \end{aligned} \quad (3.3)$$

where n is the abbreviation of n_p and the prime to it is to take the derivative with respect to z .

To eliminate the term proportional to $\partial E / \partial z$ in Eq. (3.3) we carry out a transformation

$$E = \frac{\exp \left[i \left(\frac{\omega}{v} z - \omega t \right) \right]}{\omega_p^2 - \omega^2} F. \quad (3.4)$$

By means of this we obtain the equation for F

$$\frac{d^2 F}{dz^2} + \rho F = 0, \quad (3.5)$$

where

$$\rho(z) = - \frac{(\omega \omega_b / v)^2}{\omega_p^2(z) - \omega^2}. \quad (3.6)$$

Thus in the frequency range of $\omega^2 < \omega_p^2(z)$, $\rho(z)$ is negative and growing oscillation is a solution. So far as $\rho(z)$ is a slowly varying function of position, the solution of Eq. (3.5) is obtained by means of the WKB approximation. The result is

$$F(z) = C (\omega_p^2 - \omega^2)^{1/4} \exp \left[\left(\frac{\omega \omega_b}{v} \right) \int_0^z \frac{dz}{(\omega_p^2 - \omega^2)^{1/2}} \right],$$

where C is an arbitrary constant. Here $(\omega \omega_b / v)(\omega_p^2 - \omega^2)^{-1/2}$ indicates the growth rate of the amplified wave, which becomes infinite at

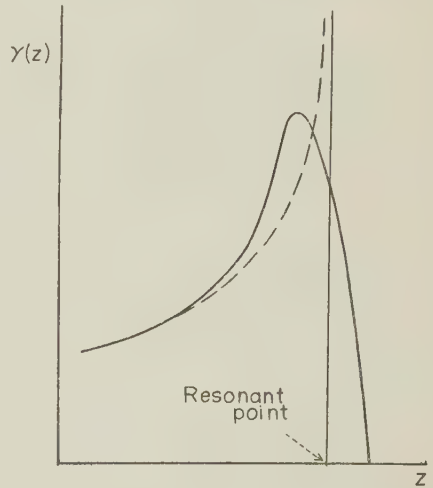


Fig. 1. Growth-rates of an amplified wave. The full line corresponds to a thermal plasma and the broken line to a cold plasma.

the point corresponding to the resonance $\omega_p^2 = \omega^2$ as shown by the broken line in Fig. 1. Thus it is clear that the growth rate increases as the wave travels down a density gradient, while decreases as the wave propagates towards an increasing density.

So far as we have discussed about the cold plasma. If the plasma has a finite temperature, we must be back to the set of Eqs. (2.25)–(2.27). If we take into account of the thermal effect, we obtain from these equations a differential equation of fourth order. It is easily seen that its solution for enough large $\omega_p^2 - \omega^2$ approaches asymptotically that for the cold plasma. For $\omega_p^2 - \omega^2$ comparable with $V_T^2 \omega^2 / v^2$, V_T^2 being the mean square thermal velocity, $\gamma \theta_p / m$, the situation is not so simple and it makes an analytical treatment of the

equation very complicated. However by considering the wave characteristics for the uniform thermal plasma which has already investigated, it is possible to infer behaviours of the wave for this case in the near region of resonance. In the uniform cold plasma the infinity of the growth rate at the resonant point is suppressed by taking into account of thermal motions in the plasma. Then the growth rate becomes finite, but a little broadened near the region of resonance. The same would be true for the non-uniform thermal plasma the real growth rate would behave like that shown by the full line in Fig. 1.

§ 4. Case of Standing Plasma Wave

As we have discussed in the preceding paper,³⁾ standing plasma waves are excited in a uniform layer with finite thickness. When the plasma has a slight non-uniformity, standing waves will also grow up in a modified form.

Here we consider only the cold plasma, since it is known that the effect of finite temperature is not remarkable unless the beam energy becomes comparable with the mean thermal energy.

To see the behaviours of standing waves we shall study the waveform by use of Eq. (3.2). In the uniform case n' and n'' vanish and the equation yields the electric field of a form of $\exp[i(k_0 z - \omega t)]$, where the wave-number k and the complex frequency $\omega = \omega_0 + i\gamma$ are constants determined by the dispersion relation. It corresponds to solve the equation as an initial-value problem. In the non-uniform case, unless effects of terms containing n' and n'' are too large, we may assume the electric field of a slightly modified form such as

$$\exp[i(\int^z k(z) dz - \omega(z)t)], \quad (4.1)$$

where the wave number k and the complex frequency ω are supposed to be slowly varying functions of the variable z . The frequency ω_0 is independent of z for standing waves concerned, while the growth rate γ varies slowly with z .

For the wave-form (4.1), we obtain

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial z}\right) E = -i(\omega - kv + v\omega' t) E. \quad (4.2)$$

Usually we are interested in the case where ω is comparable with kv ; that is to say, the

excited wave is nearly synchronized with the beam. Thus we may regard $(\omega - kv)$ as the same order of magnitude of ω or kv . Furthermore the electric field will grow up proportionally to $\exp(\gamma t)$, so that within the linear approximation γt is not far greater than unity; or $t \sim 1/\gamma$. Then the right-hand side of Eq. (4.2) can be written as

$$i(\omega - kv) \left(1 + \frac{1}{k} \frac{\gamma'}{\gamma}\right).$$

If

$$(1/k)(|\gamma'|/\gamma) \ll 1, \quad (4.3)$$

then

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial z}\right) E = -i(\omega - kv) E. \quad (4.4)$$

Similarly we get

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial z}\right)^2 E = -(\omega - kv)^2 \left(1 + i \frac{1}{k} \frac{\omega'}{\omega} - i \frac{1}{k} \frac{k'}{k}\right) E$$

which becomes

$$= -(\omega - kv)^2 E \quad (4.5)$$

if

$$(1/k)(|k'|/k) \ll 1 \quad (4.6)$$

holds in addition to (4.3). Thus by use of approximations (1.4) and (4.5), Eq. (3.2) gives the approximate dispersion relation

$$1 = \frac{\omega_p^2}{\omega^2} \left(1 - 2i \frac{1}{n} \frac{n'}{n} - \frac{1}{k^2} \frac{n''}{n}\right) + \frac{\omega_0^2}{(kv - \omega)^2}. \quad (4.7)$$

Besides, if we assume

$$(1/k)(|n'|/n) \ll 1 \text{ and } (1/k^2)(|n''|/n) \ll 1, \quad (4.8)$$

the relation (4.7) is reduced to the same form as the uniform case, which becomes

$$1 = \frac{\omega_p^2}{\omega^2} + \frac{\omega_0^2}{(\omega - kv)^2}. \quad (4.9)$$

Here it is to be noted that all inequalities (4.3), (4.6) and (4.8) would be reasonably valid if the rates of change of γ , k and n over a wavelength of the plasma wave are small enough, since k is inversely proportional to the wavelength.

To see the variation of k with z , it is necessary to solve Eq. (4.9) by taking account of the change of ω_p^2 . We suppose ω_p^2 decreasing with distance in a plasma layer with

thickness D . Then the value of $\sigma=\omega_b^2/\omega_p^2$ increases from $z=0$ to D , when ω_b^2 is kept constant. For $\sigma\ll 1$, typical curves representing the relations between ω_0 , γ and k are given in a similar way as in the reference.¹⁾

They are shown in Fig. 2, in which the curve (a) corresponds to the region near $z=0$ and (b) to the region near $z=D$. The characteristic curves are gradually deformed from (a) and (b) as the corresponding point goes from $z=0$ to D . Then it is found that for a certain frequency ω_0 the value of kv/ω_b increases from P to Q. When a standing wave is excited in this layer, the condition

$$\int_0^D k(z) dz=n\pi$$

must be satisfied. It is compared to that for the uniform case, $k_0D=n\pi$. Thus the frequency of standing wave is determined by satisfying the above condition. In such a frequency the wave-length diminishes successively towards decreasing density.

Contrary to the above, characteristic curves for the increasing density with distance move from (b) to (a), yielding more and more prolonged wave-lengths.

Now we discuss jumping phenomena of mode and frequency. As an illustration, the plasma is assumed to be uniform from A to B and thereafter have a decreasing density as shown in Fig. 3 (a). We suppose that the mode of $n=3$ starts, just when the distance from A reaches $D_3=AB$. If the plasma be uniform throughout, the jump of mode and frequency to $n=4$ would occur at the thickness

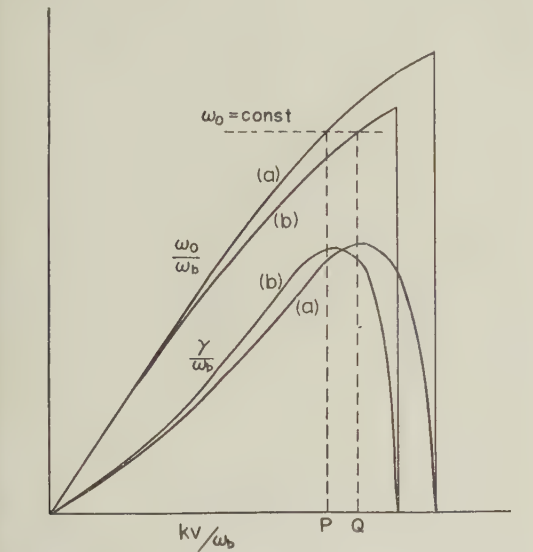


Fig. 2. Typical characteristic curves of ω_0 and γ versus k ; (a) in a higher plasma-density and (b) in a lower plasma-density.

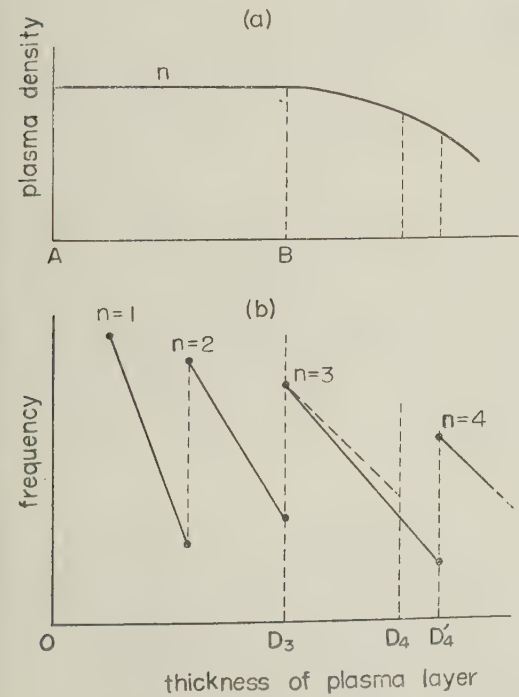


Fig. 3. (a) Spatial distribution of plasma density and (b) behaviours of mode and frequency against thickness of the plasma layer.

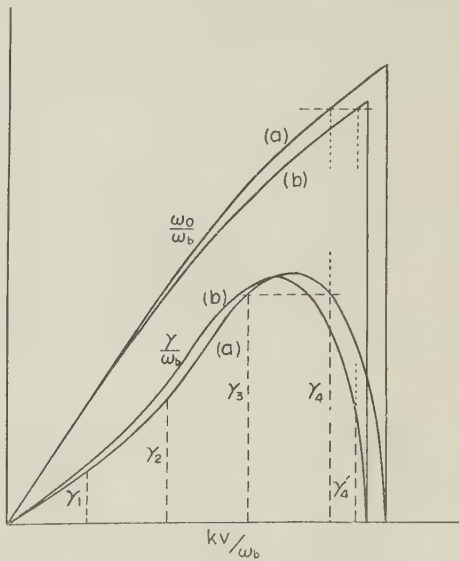


Fig. 4. An example of change of growth rate due to density variation. Curves (a) and (b) correspond to those in a uniform and a lower plasma-density, respectively.

D_4 . Then γ_4 would be just over γ_3 as argued lately.⁹⁾ However in the decreasing density, the third $1/2$ wave-length diminishes and hence the first and the second $1/2$ wave-lengths have to be prolonged. Accordingly the frequency ω_{03} is more lowered as compared with the uniform case. At the thickness of D_4 , γ_4 in the uniform region AB becomes greater than γ_3 , but in the lower-density region γ_4 is reduced to zero or a very small value γ_4' , as is seen in Fig. 4. Thus if we consider the effective growth-rate defined by

$$\gamma_{eff} = \frac{1}{D} \int_0^D \gamma(z) dz,$$

γ_{eff} for the fourth mode is still smaller than that for the third mode at the thickness D_4 . The mode-jump to $n=4$ would occur at the thickness D_4' larger than D_4 , where γ_{eff} for the fourth mode would be just beyond that for the third mode. Consequently both the increment of distance and the range of frequency-pulling within which a definite mode is maintained increase due to the decrease of density, as indicated in Fig. 3 (b).

For increasing density the opposite circumstances may be concluded.

Similar consequences for the mode-jumps will also be obtained by varying other parameters such as the density and the velocity of the beam.

It seems that the effects of non-uniformity on various features of plasma waves obtained in this and the last sections account for some experimental results,¹⁰⁾¹¹⁾ in which plasma oscillations have been observed in the region with concentration gradients.

The oscillations observed in another experiment would be also in a non-uniform region.¹²⁾ But the mechanism of exciting them is probably a little different in nature from those discussed in this paper. It will be connected with emissivity of radiation in the next section.

§ 5. Brief Discussion on Two-dimensional Case

A most simple two-dimensional case will be that all gradients of density and temperature are in the direction perpendicular to the z -axis or to the beam velocity. For instance suppose both the plasma and the beam are confined within a cylinder with a definite radius and

uniform in it. Then plasma oscillations are excited in this cylinder, but owing to the density and temperature gradients they couple with the transversal wave. This circumstance can be seen by solving the simultaneous equations (2.21), (2.26) and (2.27). We obtain an equation for transversal components with source terms arising from longitudinal component. Its solution represents, however, a surface wave travelling with the beam and decaying exponentially with distance away from the beam. Thus it turns out that the radiation from excited plasma waves cannot be emitted. This is naturally understood if we consider as follows: excited plasma waves are regarded as a row of equal electric-dipole moments with alternate directions parallel to the electric field. Therefore the radiation emitted from each dipole-moment cancels out each other at a distance of about a few wave-lengths far away from the beam and hence no radiated wave is totally observed.

If gradients of density and temperature exist in the direction slightly deflected from the beam velocity, we have a possibility of obtaining radiation which propagates nearly in the direction of gradients. This is essentially the same as what Parker and Tidman discussed in the absence of the beam.^{7) 8)}

Recently Kojima *et al.* observed radiations from a discharge-tube in which plasma oscillations are excited.¹³⁾ It is found that the radiation with about plasma frequency has a maximum intensity in the direction perpendicular to the beam velocity. This cannot be explained by the mechanism mentioned above. It seems to give a plausible explanation if we place an equivalent electric-dipole for a narrow region where the plasma oscillations exist. However, further considerations will be required for the mechanism of the equivalent dipole.

§ 6. Conclusion

We have derived macroscopic equations of linear oscillations for the system comprising a non-uniform medium-plasma and a beam.

In one-dimensional case longitudinal oscillations are independent of transversal ones regardless of non-uniformity.

As to spatially growing plasma waves, the growth rate is constant throughout the uniform

region, but it varies with distance in the non-uniform plasma. As the plasma frequency decreases and approaches the modulating frequency, a sort of resonance occurs, giving locally a rapid rise of growth rate. This is similar to the resonance in the uniform case, in which, however, the growth rate becomes very large throughout the region. As the plasma density still decreases, the growth rate falls sharply to zero soon after passing through its maximum. Towards increasing density, it is indicated that the amplitude and the growth rate monotonically decreases.

For standing plasma waves, the dispersion relation in the varying plasma density is derived under appropriate approximations. The variations of the wave number and the growth rate due to non-uniformity are obtained by considering solutions of the dispersion solution. The result is that a standing wave in a definite layer has shorter wave-lengths towards decreasing plasma-density and *vice versa*. Phenomena of jumps of mode and frequency accompanied by increasing layer-thickness are also considered. As compared with the uniform case, an increment of layer-thickness in which a certain mode jumps to the next becomes greater towards decreasing density. The range of frequency-pulling gets wider in the same process. Towards increasing density, the situations are reversed.

In two-dimensional cases we have the coupl-

ing of plasma waves and radiations. However, no satisfactory mechanism of radiation emitted from excited plasma waves has been obtained. This will require further investigations.

Acknowledgements

The author wishes to express his gratitude to Professors T. Kihara, S. Kojima and also Dr. K. Takayama for useful discussions.

References

- 1) M. Sumi: J. Phys. Soc. Japan **13** (1958) 1476.
- 2) M. Sumi: J. Phys. Soc. Japan **14** (1959) 653.
- 3) M. Sumi: Phys. Rev. Letters **2** (1959) 37; J. Phys. Soc. Japan **14** (1959) 1093.
- 4) D. Bohm and E. P. Gross: Phys. Rev. **75** (1949) 1864.
- 5) K. M. Watson: Series of Lectures on Physics of Ionized Gases, Part V (1956).
- 6) G. B. Field: Astrophys. J. **124** (1956) 555.
- 7) D. A. Tidman and E. N. Parker: Preprint of EFINS, The University of Chicago, 58-109 (1958).
- 8) D. A. Tidman: Ibid. 59-62 (1959).
- 9) T. Kihara: J. Phys. Soc. Japan **13** (1958) 473.
- 10) R. A. Bailey and K. G. Emeleus: Proc. Roy. Irish Acad. **57** (1955) 53.
- 11) D. W. Mahaffey, G. McCullagh and K. G. Emeleus: Phys. Rev. **112** (1958) 1052.
- 12) S. Kojima, K. Kato and S. Hagiwara: J. Phys. Soc. Japan **12** (1957) 1276.
- 13) S. Kojima, K. Kato, S. Hagiwara and R. Matsuzaki: J. Phys. Soc. Japan **14** (1959) 821.

Electroluminescence in Zinc Sulfide Single Crystals

By Shin-ichiro NARITA

*Institute of Electronics, Shizuoka University, Hiroswa,
Hamamatsu, Japan*

(Received June 11, 1959)

By using the vapor-phase synthesis method, zinc sulfide single crystals were grown of pure zinc and bomb hydrogen sulfide and they were doped with two impurities, copper and chlorine.

The brightness waves of E. L. in these crystals were studied by applying rectangular pulse voltage.

Since the E. L. of "*in phase*" was dominant in the crystals lacking chlorine and having appreciable voltage-dependency, it was concluded that it occurred as a result of the injection of electrons from the cathode.

In order to classify the mechanism of E. L. of "*out of phase*," infrared quenching of E. L. was used. E. L. in ZnS:Cl, Cu was typical case sensitive to the quenching, and E. L. in artificial junction (ZnS:Cl-ZnS:Cu) was the typical case insensitive to the quenching. It was supposed that the difference between these two cases resulted from the difference in the mechanism supplying the primary electrons of E. L.

§ 1. Introduction

Since Destriau's discovery¹⁾ in 1932, many workers have carried out various kinds of investigations in the field of electroluminescence. In the early days, light panels made by suspending the luminescent powders in dielectric mediums and by holding them between transparent conductive pieces of glass and aluminium electrodes, were generally used. This method was inadequate for studying the mechanism of electroluminescence (hereafter being denoted as E. L.), because the dielectric mediums had a considerable effect on E. L. and the contact between the particles had to be taken into consideration.

Piper and Williams²⁾ first conducted investigations on the single crystals of ZnS and they reported many excellent results. The fundamental idea of the barrier theory, proposed by them and ascertained experimentally by Neumark³⁾ and Cusano,⁴⁾ has been supported to this day. According to this theory, electroluminescence takes place by the impact ionization of luminescent centers by the fast conduction electrons accelerated by the high electric field at the barrier, and by the recombination to the luminescent centers of the multiplied electrons. This conception was supported experimentally by the voltage-dependency of the brightness of E. L. The most interesting problem in dealing with E. L.

is that concerning the brightness waves against the time-varying exciting voltage. The prominent brightness of emission occurs at the voltage-drop and is generally called the "secondary peak." Zalm, Diemer and Klassens,⁵⁾ Haake,⁶⁾ and other investigators considered this phenomenon to be a trapping effect. Also, the emission of light "*in phase*" against the applied voltage was investigated by Frankl⁷⁾ and others.

In spite of these investigations, the phenomena of E. L. are considered to be very complicated and largely affected by the kinds of impurities contained. Moreover, the problems of barrier, luminescence, electron multiplication, trap, etc, are related to each other, so that many unsolved questions concerning E. L. still remain. One such problem is the question as to where the primary electrons to be accelerated are supplied.

In this paper, from the data obtained on ZnS single crystals doped with Cu and Cl, by applying rectangular pulse voltage, some discussion about the problems is attempted.

§ 2. The Preparation of ZnS Single Crystals

Generally, single crystals of ZnS have been made by the vapor-phase methods. One of these, performed by Kremheller⁸⁾ and others,⁹⁾ is the method of sublimation using pure ZnS powder. The other, which was used by

Frerichs¹⁰⁾ and Bube¹¹⁾ for manufacturing CdS or ZnSe, is known as the vapor-phase synthesis method.

The latter method, together with several device aimed at improving it, was adopted in this experiment. The structure of the furnace is shown schematically in Fig. 1. In regard to the furnace, special attention was paid to the introduction of zinc vapor and H₂S gas. The temperature of the pure zinc to be vaporized was held at 700°~800°C, and at the same time argon gas was passed over the molten zinc carrying the zinc vapor to the outlet of the leading tube, where H₂S gas mixed with refined nitrogen was expelled from the other tube.

The single colorless crystals of zinc sulfide grew and gathered thickly at the outlet of

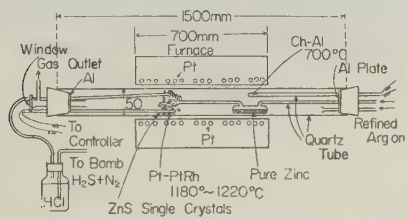


Fig. 1. Furnace for the growth of ZnS single crystals.

the leading tube. The representative dimensions of the plate-like crystals were about 1.5 mm in width, 6~7 mm in length and about 0.2 mm in thickness, and those of the bar-type crystals were 0.7~1mm in diameter, and 1~2 cm in length.

For the purpose of doping these crystals with chlorine, the mixture of H₂S and N₂ gases was passed through hydric chloride, while for doping with copper the crystals were immersed in a water solution of CuSO₄ after which they were heat-treated at 500°C in a furnace.

§ 3. The Relation between the Impurities contained and the Photoluminescence and Electroluminescence of ZnS Crystals

As mentioned above, the single crystals grown by vapor phase synthesis, were colorless and transparent, and the physical data gathered on these crystal always exhibited the characteristic property of the impurity contained. The relation is tabulated on Table 1.

The term “in phase” in the table means the electroluminescence emitted in the same phase of the applied voltage and the term “out of phase” means that of having phase-displacement from the exciting voltage. If

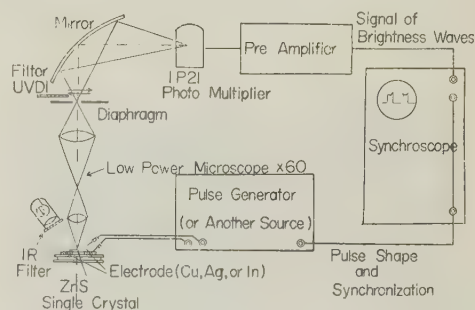


Fig. 2. Schematic diagram of the apparatus for measuring the brightness waves of E.L.

the voltage is of the rectangular pulse type, “out of phase” emission can be observed at the rise or fall of the pulse.

The term “With or Without UV” is used in classifying whether or not the E. L. contains ultraviolet emission (3500Å~4000Å).

§ 4. Measurement of the Brightness Waves

In the study of E. L. the wave shapes of the emission from ZnS single crystals, corresponded to the exciting time-varying voltage, are frequently used, and called brightness waves.

Table I. P. L. and E. L. of ZnS single crystals.

Crystals	Photoluminescence	Electroluminescence	
		“In Phase”	“Out of Phase”
Pure	No	No	No
Doped with Cu	No or Very Weak	Yes with U. V.	Yes Very Weak
Doped with Cl	Strong Blue or Yellow	No	No
Doped with Cl, Cu	Strong Green or Blue	Yes without U. V.	Strong Blue or Green

A pulse generator used in the experiment has a rise time of a few microseconds, a duration variable from several microseconds to a hundred milliseconds and a repetition rate variable from several cycles to several kilocycles, and its voltage varies from 0 to 2600 volts positively. Other source of supply were also used, e.g., 60 cycle half-wave, sinusoidal voltage of variable cycles and D.C.

The emission intensity from ZnS single crystals was measured with a photomultiplier, 1P21, after it passed through a low power microscope and sometimes also through a Matsuda UV-D1 filter (which is transparent in the range of $3200\text{\AA} \sim 4000\text{\AA}$). Subsequently it was observed with a synchroscope. The general features of the apparatus are shown in Fig. 2.

§ 5. Comparison of the Brightness Waves obtained by Applying the Pulse Voltage to those by the Voltage of 60 cycle Half-waves

Up until now sinusoidal waves and 60 cycle half-waves have been mainly used in the measurement of brightness waves. The comparison of wave forms obtained by pulse voltage to those obtained by the conventional method is not always possible, but the principal features are shown in Photo 1.

§ 6. E. L. from ZnS Single Crystals doped with Copper Impurity alone

With crystals grown by the vapor-phase reaction method, E. L. could not be observed

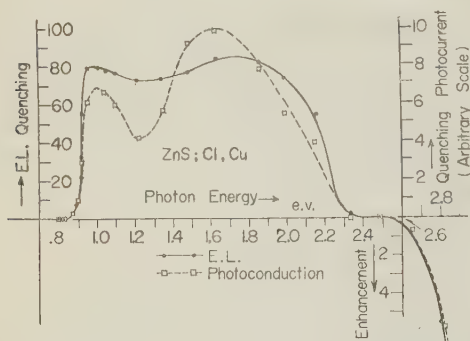


Fig. 3. Spectral distribution of quenching light for E.L. and photoconduction.

so long as the crystals were not doped with any impurity, but from the crystal treated to contain copper a weak emission was observed.

The brightness waves in this case were

mainly "in phase," the emission being noisy and decaying rapidly (it was impossible to observe the decay time, which was perhaps about $1\mu\text{sec.}$), and contained ultra-violet light which was thought to be the edge emission. Photo. 2. is an example of this case. The voltage dependency of the emission intensity was larger than in the other cases shown in Fig. 4.

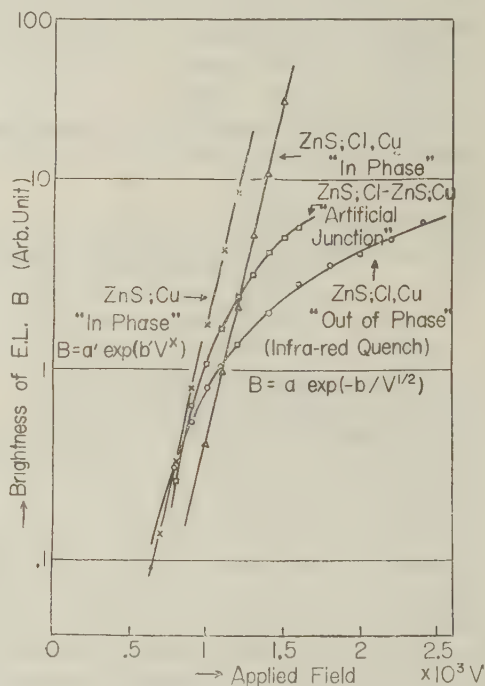


Fig. 4. Voltage-dependency of the brightness of E.L.

The weak "out of phase" emission also appeared and the time constant of the decay was about $50 \sim 70\mu$ seconds.

§ 7. E. L. Emission from ZnS:Cu, Cl. (Case of Infrared Quenching)

Although in Section 5 the E. L. has been classified by the phase of brightness wave compared with the exciting voltage, it may be more advantageous for studying the mechanism of E. L. to classify E. L. according to whether or not it is affected by the infrared light.

The single crystals having emissions easily reduced by infrared irradiation, were obtained by doping them with chlorine during the crystal growth and baking them in a furnace after immersing in an aqueous solution of CuSO_4 in order to add the copper impurity.

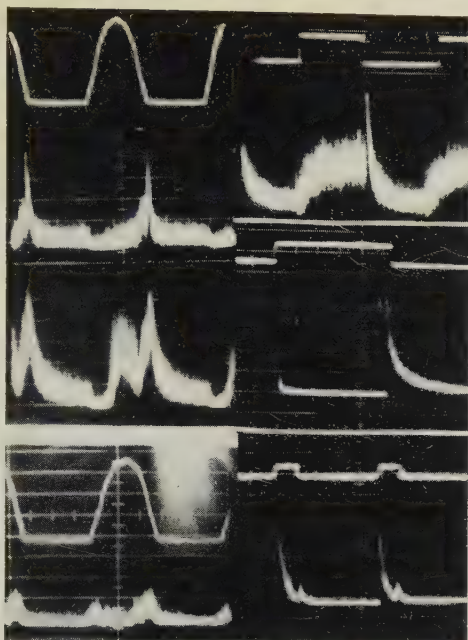


Photo. 1. Comparison of the brightness waves obtained by applying voltages of 60~ half wave, and those of rectangular pulse. Left side (60 cps half wave): Top, wave form. The next two show the oscillogram of E.L. of "out of phase" at the voltage-drop and that of "in phase" plus "out of phase". Next, wave form. The bottom shows E.L. of "out of phase" at the voltage rise plus that of at the voltage-drop. Right side (rectangular pulse): Top, wave form and E.L. of "in phase" plus that of "out of phase" at the pulse fall. Middle, wave form and E.L. remarkable at the pulse fall. Bottom, wave form and E.L. remarkable at the pulse rise. (Time markers are at intervals of 100μ sec.).

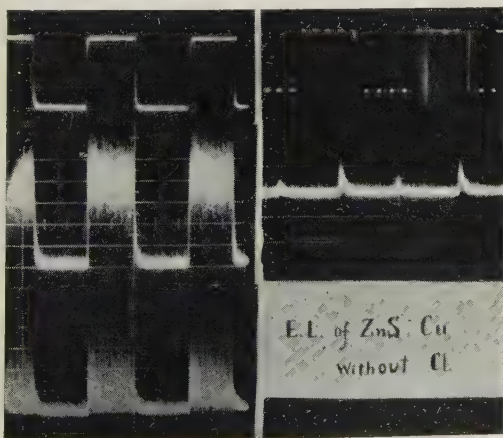


Photo. 2. E.L. of ZnS;Cu without Cl. Left side; wave form and noisy brightness waves of E.L. of "in phase". Right side; wave form and weak brightness waves of E.L. of "out of phase". (Time markers are at intervals of 100μ sec.).

The infrared quenching of E. L. takes place slowly under weak infrared irradiation and does not recover rapidly unless irradiated by violet or ultraviolet light.

In Photo. 3, the top two photographs show microscopic views of the sample before (left) and after (right) the infrared irradiation. The photos on the lower left hand side subsequently show the aspects of reduction of the brightness waves at the part of the crystal affected by infrared light and the photos on the lower right hand side show the invariant brightness waves of E. L. in the several small parts where quenching does not occur.

The wave shapes on the left hand side of Photo. 4. show the variation of the current throughout the crystals before and after the

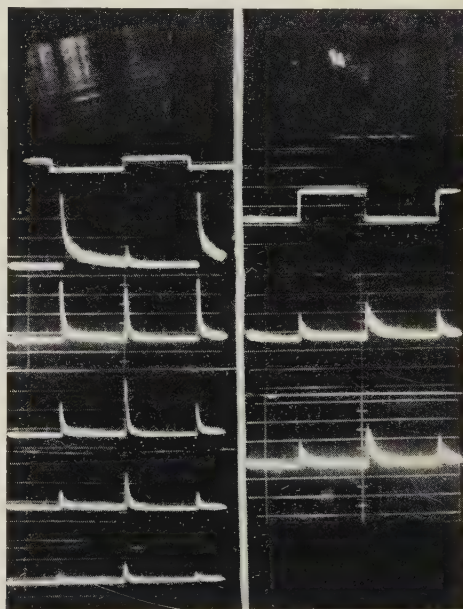


Photo. 3. Infrared quenching on E.L. of ZnS;Cl, Cu. Left side: (Top) microscopic view of E.L. before the infrared irradiation, (Below) wave form, the brightness wave of E.L. before quenching and the aspect of the quenching of E.L. gradually by the infrared irradiation*. Right side: (Top) microscopic view of E.L. after the infrared irradiation, a small part of which is remains unaffected by the infrared light, and the lower photos indicate the invariant quality of E.L. both before and after irradiation. (Time markers are at intervals of 100μ sec.).

* The reason for the occasional temporary increase in "the first peak" of E.L. at the pulse rise remains unknown.

infrared quenching by applying rectangular type pulse voltage, and those on the right hand side show the changes caused by the temperature rise.

Though the instant kicks of current corresponding with the rise and fall times of the applied pulse-voltages are invariant before and after infrared quenching, a DC-like flow of current was observed during the application of pulse voltage before the quenching, and disappeared after the infrared quenching.

The spectral distribution of quenching effect

added in the figure under the zero line of the coordinate.

It is suggested by the similarity of the energy range of the infrared quenching of E. L. to those of the photoconductivity of ZnS:Cl, Cu crystals that both of them are of the same origin, that is, the destruction of the action of the sensitizing centers in the crystals by the infrared irradiation.

This will be discussed in detail later.

The remarkable aspect in this case is the considerable change of the position of the light-emission and of the shapes of the bright-

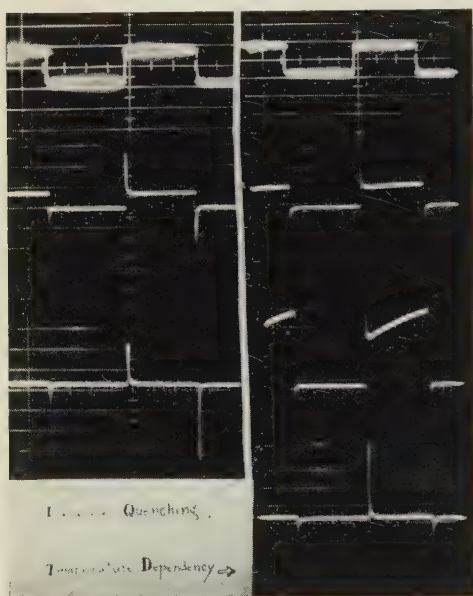


Photo. 4. The infrared quenching and the temperature dependence of the current throughout ZnS single crystals in the case of the quenching of E.L. Left side: Top, wave form, Below, the current waves before and after the infrared quenching. Right side: Top, wave form, Below, the current wave forms at 25°C, 75°C, and about 120°C.

(Time markers are at intervals of 100 μ sec.).

for E. L. is shown in Fig. 3. together with that for infrared quenching of photoconduction on the same ZnS:Cl, Cu single crystals. The ordinate scales indicate the E. L. quenching percent and the reduced photocurrent in the arbitrary scale for the constant amount of the incidental light having the photon energy shown in the abscissa.

The enhancement rather than the quenching of emission and conduction was observed at the energies above 2.5 e.v. as they were

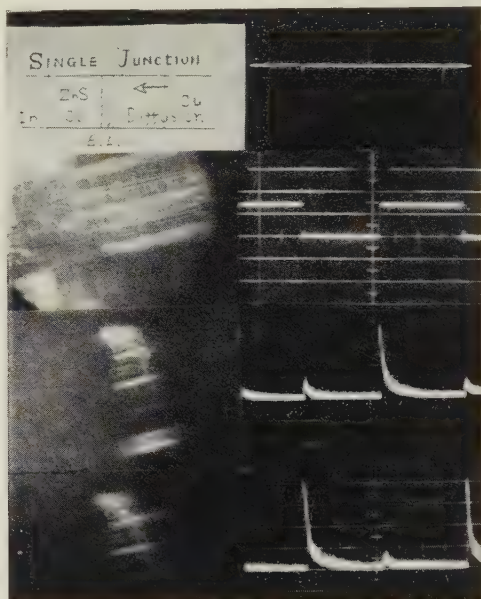


Photo. 5. Electroluminescence of artificial junction produced by the diffusion of copper from one side of the crystal. Left side: the upper photo indicates the microscopic view of the crystal and those below are microscopical views of E.L.—in the middle photo the copper electrode was minus, and in the bottom photo the copper was plus. Right side: the top photo shows the current waves passing through the crystal; the next shows the pulse wave form; and the lower two show the brightness waves corresponding to the respective photographs to their left.

(Time markers are at intervals of 100 μ sec.).

ness waves when the direction of the applied field was inversed. This forms a good contrast with the case described next.

§ 8. E. L. from ZnS:Cl-ZnS:Cu (Case of Artificial Junction)

A representative example of E. L., not af-

fect by infrared irradiation, was that of artificial junctions.

Single crystals of ZnS:Cl (without Cu), which were believed to be *n*-type, were employed as the base of the artificial *p-n* junctions. Copper, evaporated in vacuo, was added to one side of each crystals, and then the crystals were heat-treated in a furnace of 500°C for 30 minutes in a flow of argon. In each crystals by the diffusion of copper during this treatment the *p*-side of the junction was created. After then electrodes were fixed at both sides of the crystals to measure the E. L.

Photo. 5. contains the microscopic views of E. L. radiation both in the cases of making copper (*p*-side) minus and indium (*n*-side) plus, and in the reverse case.

Also, this photo contains the brightness waves in both cases and the wave shapes of the current flow (shown on the top right hand side of the photo).

In the artificial junction, the luminant position of the crystal is made invariant by reversing the direction of the current, and brightness waves were recorded mainly at the rise time of the pulse voltage when the copper electrode was minus, and at the fall time of the pulse when the copper was plus.

These facts show that the direction of the instant kick of the current, which make the barrier steeper, is the effective direction which causes E. L. in the crystals.

By studying the current wave it becomes clear that the current through the crystal does not contain the stationary DC-like component.

In the case it is also shown that little change of E. L. takes place by inserting, in series, a condenser of scores of micro-microfarads to the circuit.

This result gives substantial evidence to the theory that the junction in the crystal acts in the same way as does a small condenser.

Fig. 4. presents the relation between the brightness of the emission and the applied pulse voltage.

In the case of infrared quenching, brightness, B , is known to be well-fitted to the formula,

$$B = a \exp(-C/V^{1/2}) \quad (1) \quad \text{and}$$

where a and C are constants and V the appli-

ed voltage. On the other hand in the case of artificial junction the experimental formula is

$$B' = a' V \exp(-C'/V^{1/2}) \quad (2)$$

where a' and C' are the other constants and the brightness is known to have a more intense voltage dependency.

The "in phase" brightness of E. L. has more intense voltage dependency than the "out of phase" brightness as shown in the figure in samples of both ZnS; Cu and ZnS; Cu, Cl.

The fact that ultra-violet light which is believed to be the edge emission was contained only in "in phase" E. L. radiating from ZnS; Cu, but not from ZnS; Cu, Cl, was explained by the difference in the number of the luminescent centers.

§ 9. Discussion

Barriers such as rectifying layers between *p*- and *n*-type ZnS or between Cu₂S and ZnS in or on the surface of the ZnS single crystal are apt to be produced by doping the crystal with the copper impurity. The existence of these barriers, therefore, is considered as the requisite for E. L.

The electric field must be concentrated in the barrier, when the voltage is applied in the reversed direction. According to Piper and Williams, the primary electrons existing previously in the conduction band are accelerated by the strong field at the barrier and are multiplied by the impact on the luminescent centers.

The validity of this theory is proved by the fact that the voltage dependency of the brightness satisfies the formula (1) already described

$$B = a \exp(-C/V^{1/2}) \quad (1)$$

Also, according to the conception of Haake and other investigators, the electrons excited by the impact ionization of luminescent centers are temporarily trapped in the traps and return to the original luminescent centers by being released thermally from the traps after the removal of the exciting voltage. Assuming that the recombination process is a one-molecular reaction, the brightness of the emission is expressed by the formula

$$B = B_0 \exp(-t/\tau)$$

$$\tau = 1/s\{\exp(E/kT)\}$$

where τ is the decay time, s the frequency factor (which may be assumed to be 10^{-10}sec.^{-1}), E the depth of the traps from the bottom of the conduction band, K Boltzmann's constant, and T the absolute temperature.

With the above in mind the decay curves of the E. L. of several "out of phase" components were plotted in logarithmic scale against the time as shown in Fig. 5.

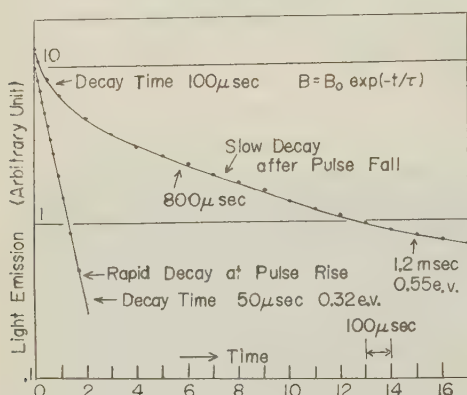


Fig. 5. Decay curves of the brightness in E.L. of "out of phase".

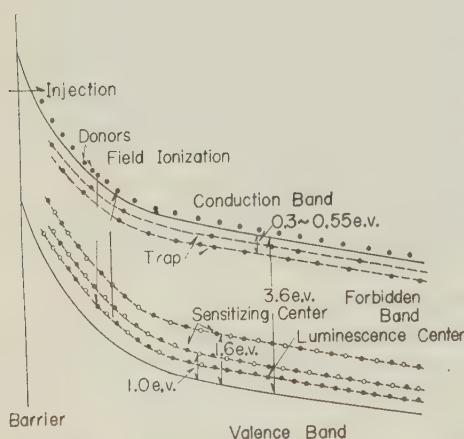


Fig. 6. Energy level diagram for ZnS single crystals having barriers.

When the infrared quenching is studied, the decay time of the brightness waves at the fall time of the pulse is longer than that at the rise time. This effect may be explained by the fact that the flowing time of the charge carriers through the bulk of the crystal before the emission is much longer at the fall time than that at the rise time, so that the several kinds of deep traps are filled which may otherwise have only a slight probability of capturing electrons and therefore

vacant. On the contrary, at the rise time of the pulse the emission was thought to be produced by the instant current through the crystals (the greatest part of which was supposed to be produced by the field ionization of donors), and therefore, the decay time of the brightness waves is related only to the shallow traps (supposed to be about 0.32 e.v. below the bottom of the conduction band), becoming as short as 100 μ sec. or less.

The following discussion, referring to the energy level diagram in Fig. 6., is offered.

(1) *The interpretation of the infrared quenching*

The difference between the case in which the emission of E. L. is and is not quenched by infrared light may be attributed to the mechanism used in supplying the primary electrons before the impact of the electrons on the luminescent centers or other centers.

As shown in Fig. 3. the energy of the irradiated light causing the quenching of E. L. corresponds to that of photoconductivity, and the crystals in which E. L. is easily quenched by infrared light, have several times more photoconductivity than the other crystals. These facts confirm the important role of the sensitizing centers in the crystal on the electroluminescence.

The similar fact has already been pointed out by Bube¹¹⁾ and Rose¹²⁾ in the case of CdS crystals, where the photoconductivity of the crystals is sensitized by the sensitizing centers.

According to their theory, for the sake of the existence of the centers, the conduction electrons which are previously excited by photons or electrons, come to a longer life time and the CdS crystals become more photoconductive.

In a similar way, in the electroluminescence of ZnS, the electrons, being excited by photons or other electrons and raised to the conduction band, become to have a longer life time, through the assistance of the sensitizing centers, and become the primary electrons of E. L. and impact-ionize the luminescent centers under the strong electric field at the barriers and cause the electron multiplication which results in the strong radiation of E. L.

Furthermore, in the crystals irradiated by infrared light, the holes trapped in the sensitizing center are excited down to the filled band and are recombined with the conduction

electrons, thereby reducing the number of the primary electrons and thus causing the weakness of the E. L. (as in photo. 3.) and the simultaneous disappearance of the DC-like current through the crystal (as in photo. 4.).

Besides, the fact that this spectral distribution of the infrared quenching of E. L. corresponds closely with that of the infrared radiation under ultra-violet irradiation which Browne¹³⁾ observed, seems to suggest that the sensitizing centers should be those acceptors which are made of copper impurities.

(2) *The emission from the artificial junction*

In contrast to the above-mentioned it should be taken into consideration that in the case where no quenching by the infrared irradiation occurs, for example, as in the case of the artificial junction the electroluminescence cannot have any relationship to the sensitizing center, and, in this case, it may be supposed that the barrier acts as a condenser in the crystal and the polarization current flows instantaneously through the crystal at the rise and the fall of the applied pulse.

The charge and discharge of the condenser are synonymous with the electron capturing by the vacant donors and the field ionization of the filled donors in the barrier region and with the supply of the primary electrons from the donors to the conduction band during the process, and after the instant current at the rise and fall of the pulse, the preexcited electrons may return from the traps to the luminescent centers and emit a strong luminescence.

It can be understood from the theory of p - n junctions that a strong electric field is produced in the barrier, when the direction of the current is that of "hard flow", namely, flowing from the n -side to the p -side. In the artificial junction the above condition which is effective for E. L. is realized at the fall time of the applied pulse when the copper electrode is set positive and the other side negative, and also at the rise time of the pulse when the copper electrode is set negative, because in both cases the direction of the instant current flow becomes that of "hard flow". (Refer to the current waves in Photo. 5.).

The shapes and phase of the brightness waves in photo. 5. support the above theory.

Also, the invariance of the brilliant posi-

tion of E. L. in the crystal, caused by inverting the applied pulse, is a proof of the consideration that the light of E. L. is emitted from the same barrier in spite of reversing the direction of the pulse voltage.

Moreover, the lack of stationary DC-like parts on the current waves is an evidence of the instant flow through the barrier-capacitance as the field ionization of the donors. Also, the invariability of E. L. even after inserting a series condenser in the circuit may also be another evidence for this conception.

Conversely, in the case of "infrared quenching", the reversal of the direction of the electric field changes the region, and the brightness of E. L. in the crystal, that is to say, the brightness at the cathode is often stronger than at the other parts.

(3) *Explanation of the voltage-dependence of "out of phase" E. L.*

As shown above, in the case of "infrared quenching" the experimental formula

$$B = a \exp(-C/V^{1/2})$$

coincides well with the conventional theories.

In the case of "artificial junction" the consideration that the primary electrons are produced by the field ionization must lead to the other formula which depends more strongly upon the applied voltage than the former, namely, in its experimental form,

$$B = a' V \exp(-C'/V^{1/2})$$

(4) *The case of "in phase" E. L.*

In addition to the above mentioned, the primary electrons may be supplied by the injection from the electrodes or the exterior of the barrier in the crystals. It may be assumed that this is a case of "in phase". It is evident also in this case, that for the strong emission the process of the impact excitation must be contained in the E. L. mechanism.

As the injection of electrons from the exterior of the barrier is considered to have the need of appreciable field intensity (such as in the case of field emission), the voltage dependency of the brightness becomes strong as shown in Fig. 4.

The electrons thus injected cause the luminescent centers or other levels to become vacant due to the impact ionization where the electrons injected in succession may fall in and photons are emitted as E. L. These processes are apparently in phase against the

applied voltage and mostly independent of the traps, and E. L. accompanying them may have such a rapid decay time that it cannot be observed (as in photo. 2.).

In this case the factor determining the required voltage to produce E. L. is mainly the energy which is necessary for the injection of electrons from outside the barrier, so that the voltage dependency may be as severe as that shown in the experimental formula which is proportional to the exponential of $bV^{1/2}$ rather than to that of $(-C/V^{1/2})$. Moreover, in the case of "in phase" E. L. the process of the electrons flowing through the barrier brings about a complex variation in the phenomena, namely, causing the luminescence to become noisy or producing the sudden appearance of "in phase" emission by raising the temperature.

It was concluded from the weakness of the photoluminescence of ZnS; Cu without Cl crystals by the irradiation of 3650Å that few luminescent centers exist in the crystal. Therefore the impact ionization may possibly proceed by exciting the electrons in the valence band and raising them up to the conduction band, and the recombination of conduction electrons and holes in the valence band may be executed directly. These mechanisms can easily explain the fact that the E. L. of the crystal (ZnS; Cu) contains the ultra-violet light corresponding to the edge emission of ZnS, (the peak of which is at about 3700Å).¹⁵⁾

The difference between Smith's observation¹⁵⁾

of the edge emission in E. L. of ZnS and Frankl's denial⁷⁾ of the existence of the emission may be explained by the difference in the quantities of impurities contained in ZnS single crystals.

Acknowledgement

The author would like to express his sincere thanks to Dr. T. Horii for his kind encouragement. The author's thanks are also due to Messers. K. Takagi and S. Yamada for their helpful discussion and to Mr. K. Nakanishi for his laborious assistance.

References

- 1) G. Destriau: J. chem. phys. **34** (1937) 117, 327, 462.
- 2) W. W. Piper and F. E. Williams: Phys. Rev. **81** (1952) 151.
- 3) G. F. Neumark: Phys. Rev. **103** (1956) 41.
- 4) D. A. Cusano: Phys. Rev. **98** (1955) 546.
- 5) Zalm, Ziemer, and Klassens: Philips Res. Repts. **9** (1954) 81.
- 6) C. H. Haake: J. Opt. Soc. Amer. **47** (1957) 881.
- 7) D. R. Frankl: Phys. Rev. **100** (1955) 1105.
- 8) A. Kremheller: Sylvania Technologist **8** (1955) 11.
- 9) T. Matsumura, H. Fujizaki, Y. Tanabe: Bull. Res. Inst. Sci. Measur. Tōhoku Univ. **7** (1958) 29. (in Japanese)
- 10) R. Frerichs: Phys. Rev. **72** (1947) 594.
- 11) R. H. Bube: Phys. Rev. **99** (1955) 1105.
- 12) A. Rose: RCA Review **12** (1951) 362.
- 13) Refer to the next paper.
- 14) R. E. Halsted, E. F. Apple and J. S. Prener: Phys. Rev. Letters **1** (1958) 134.
- 15) R. W. Smith: Phys. Rev. **100** (1955) 760.

Electron Microscope Study of the Decomposition Process of Oxide Coated Cathodes

By Shoichi HIROTA and Tetsuji IMAI

Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokyo, Japan

(Received August 13, 1959)

Electron microscope observation on oxide coated cathode is undertaken especially on its decomposition process and on the prolonged heat treatment.

A new replica method which is used in this study is as follows; (1) deposition of SiO film at first on the specimen, (2) pressing the SiO-evaporated-specimen onto ethylmethacrylate resin film, (3) shadowing by germanium evaporation and (4) reinforcing with carbon film. This replica technique enables us to observe the exact surface structure of oxide cathode, which has a porous surface and which is very unstable in the atmosphere.

About the decomposition process, following results are obtained: Growth of the oxide crystal becomes significant at a certain decomposition-temperature. For "triple carbonate", this critical temperature lies at around 1100°C. With the "single carbonate", crystal growth occurs at considerably lower temperature than with the triple.

§ 1. Introduction

Many studies have been made on various aspects of the oxide coated cathode during these fifty years since its discovery by A. Wehnelt. One of the most interesting fields of the investigations of oxide cathodes may be the correlation between cathode activity and particle size or crystal size of carbonates and oxides. Carbonates such as BaCO_3 , $(\text{BaSr})\text{CO}_3$, and $(\text{BaSrCa})\text{CO}_3$, used as emission paste are stable in the air and not only optical microscope observations but also electron microscope observations¹⁾ of it have been done. Concerning the oxide crystal, only an X-ray diffraction method has been used especially in connection with the crystal growth of oxides²⁾⁻⁶⁾.

We have attempted to observe the crystal growth of oxides by an electron microscope. The main difficulties, which we have encountered in the electron microscope study of oxide cathode, exist in preparing a suitable replica, owing to extremely porous structure of the oxide coating and its chemical instability in the atmosphere. Yazawa et al⁶⁾ have tried to get a replica of the oxide in vacuum by a simple SiO-evaporation method, of which resolution was rather poor. By a special technique, we succeeded to prepare a suitable replica of the oxide coating without any

formation of carbonates or hydrates and it enabled us to obtain an electron microscope image of a real surface of the oxide coating with considerable resolution. In this paper,* electron microscope observation are presented, both of the thermal decomposition process of cathode coatings from carbonates to oxides and of prolonged heat treatment effect after decomposition.

§ 2. Experimental Method

A. Experimental specimens

Emission pastes which are used in the present study are "triple carbonate", $(\text{Ba Sr Ca})\text{CO}_3$ ($\text{Ba Sr Ca}=47:43:10$) and "single carbonate", BaCO_3 ; both are prepared from nitrates by a precipitation with sodium carbonate. The carbonate is coated on a pure nickel flat sleeve ($32\text{ mm} \times 2\text{ mm} \times 0.8\text{ mm}$) by an ordinary spray method to a thickness of about 50 microns.

Heat treatment of these carbonates is undertaken in an evacuating system at five points of temperature, i.e., 700°C, 850°C, 950°C, 1100°C and 1250°C for 3 to 60 minutes until appreciable outgassing is completed at each temperature. Temperature and time-

* The following results have been outlined at the Meeting of the Society of Applied Physics, Japan in 1957.

length of heat treatment are given in Table I associated with the final vacuum degree at the end of the heat treatment. Temperature values in Table I indicate measured values at the sleeve metal using Pt-RtRh thermocouple, therefore the surface temperature of the coating should be lower than that given in Table I by an amount 50°C or so.

In order to clarify the effect of prolonged heat treatment after decomposition, continued heating is imposed upon the triple oxide which has finished its decomposition process. Temperature at decomposition and at continued heat treatment and time-length of heat treatments are given in Table II.

Table I.

Specimen No.	Decompositions		Final Vacuum degree mm Hg
	Temperature °C	Time min	
1a(Triple) 1a(Single)	700	60 60	3×10^{-6}
2a(T) 2b(S)	850	15 15	1×10^{-6}
3a(T) 3b(S)	950	5 15	1×10^{-6}
4a(T) 4b(S)	1100	3 8	5×10^{-6}
5a(T) 5b(S)	1250	3 3	5×10^{-6}

Table II.

Specimen No.	Decomposition Temperature °C	Heat treatment	
		Temperature °C	Time min
6a(Triple) 7a(T)	850	850 850	5 5

B. Electron microscopic replica technique

Details of our replica technique is reported elsewhere⁷⁾, and only some outlines are mentioned here. In an evacuating system, deposition of SiO is made at first on the specimens which have finished the above mentioned heat treatments. Two tungsten coils in which a few milligrams of SiO is inserted are so located above the specimen, that depositions of SiO are made obliquely at the same incident angle from opposite direction. Next, air is introduced in the system very slowly. Then, the specimens with SiO film are molded

on a resin which is preheated at about 120°C so slightly that the resin does not penetrate deeply into the specimen particles. After removing the oxide coating from the resin by dissolving with dilute nitric acid, the SiO replica is shadowcasted with germanium vapor. Further, carbon is vaporized so as to link up each pieces of the replica film on the resin, because the replica consists of very small pieces owing to the extreme roughness of the specimen surface and hence could not be mounted on the specimen screen. Before scooping up the replica on the mesh, the resin under replica is dissolved away with acetone.

§ 3. Experimental Results

A. Thermal treatment of carbonates

A-1 Triple Carbonate

Electron microscope image of triple carbonate before any heat treatment and those of the specimens 1a, 2a, 3a, 4a, 5a given in Table I are shown in Fig. 1 to Fig. 6. From this series of photographs, following points may be stated.

(i) The specimen for which heat treatment is undertaken at 700°C indicates no essential change both in shape and in surface structure of each particle (Fig. 1 and Fig. 2).

(ii) Heat treatment at 850°C produces considerable change at the surface of each particle as shown in Fig. 3. The smoothness of surface which we find in Fig. 1 and 2 disappears and considerable roughness is seen.

(iii) As shown in Fig. 4, many crystallites of very small size come out uniformly all over the specimen particle surface by the heat treatment at 950°C. These fine crystallites may be considered as new crystallites grown by heat treatment and the size of these new crystals are estimated as about 500Å on the average.

(iv) By the heat treatment at 1100°C, each fine crystallite on the specimen surface becomes a little larger in size and the crystal growth takes place to more extent compared with Fig. 4 as illustrated in Fig. 5.

(v) it will be noticed that the shape of specimen particles is not appreciably changed from that of untreated carbonate by the above mentioned heat treatments as shown in Fig. 1~5. The specimen, however, when subjected to a heat treatment at 1250°C, indicates

extensive crystal growth and the particles link up with each other. This will be seen in Fig. 6 and it is difficult to decide the original shape of each carbonate particle from this image. The size of new crystallite grown in each particle may be estimated as large as 1 micron in this case.

A-2 Single Carbonate

Electron microscope images of single carbonate before any heat treatment and those of the specimen 1b~5b given in Table I are shown in Fig. 7 to Fig. 12. As seen in Fig. 7, each particle of BaCO_3 has a calcite type crystal structure with a length of each side of about 0.5 micron. Through the heat treatment at 700°C , the edges of calcite structure become somewhat round and at the same time even the adjoining of particles occurs as indicated in Fig. 8. Such tendency becomes very remarkable when heat treatment is undertaken at 850°C (Fig. 9). When further heating is made at 950°C , some projections begins to appear, which are considered as new centers of crystal growth, while no drastic change in the shape of particles takes place. This may be easily found in comparison between Fig. 9 and Fig. 10. As the heat treatment is carried out at higher temperature, as at 1100°C and 1250°C , such a crystal growth is enhanced more intensely as we can find in Fig. 11 and Fig. 12. It is clearly seen from these photographs that the crystal growth takes place in laminar structure.

B. Thermal Treatment of Oxide Coatings after Decomposition

In Fig. 13~Fig. 14, images obtained for the specimens 6a~7a in Table II are shown. For the specimen 6a, for which heat treatment has been undertaken at 850°C and for which the continued heating is imposed further at 850°C for 5 hrs, Fig. 13 which resembles Fig. 4 is obtained. Only difference between Fig. 4 and Fig. 13 is the difference in the size of fine crystallites which are found on the surface of the specimens. The size of fine crystallites in Fig. 4 is larger than that in Fig. 13 by a factor of about 2. If the decomposition of the carbonate has been done at 1100°C , Fig. 14 is obtained, which is very different from Fig. 13 in spite of the same condition of the prolonged heat treatment, i.e. 850°C and 5 hrs. In this case, crystal growth

takes place stratifically to a size as large as 1 micron, rather resembling the specimen 5a in Fig. 6 mentioned above.

§ 4. Discussions

According to the study made by Eisenstein²⁾ with X-ray diffraction method on the decomposition process of $(\text{BaSr})\text{CO}_3$, (1) crystal



Fig. 1. Electron micrograph of $(\text{Ba}\cdot\text{Sr}\cdot\text{Ca})\text{CO}_3$ before thermal decomposition.



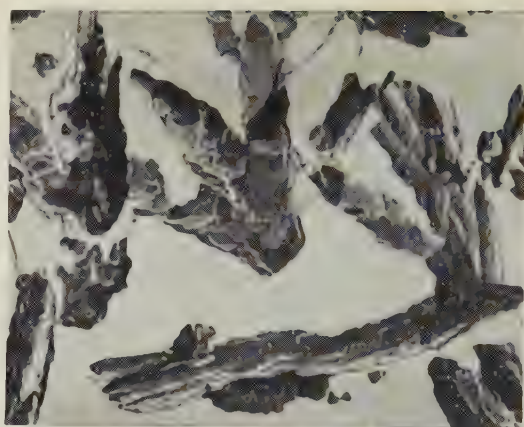
Fig. 2. Decomposition condition: 700°C for 1hr., in vacuum.

growth of carbonate begins at about 700°C , (2) crystal of BaCO_3 remains even after heat treatment at 795°C for 2 min., (3) crystal growth of oxide solid solution $(\text{BrSr})\text{O}$ begins at about 1000°C and (4) through the heat treatment at 1050°C for 5 min., crystal size



1 μ

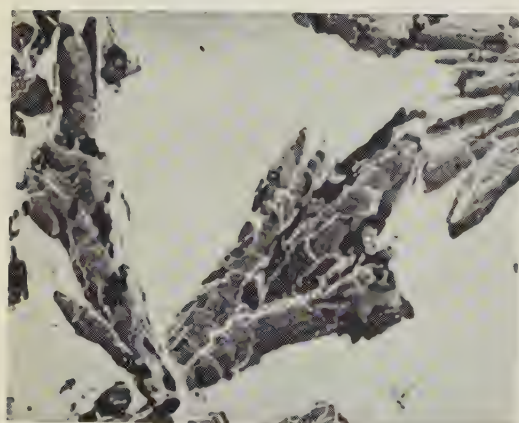
Fig. 3. 850°C 15 min.



(1)

1 μ

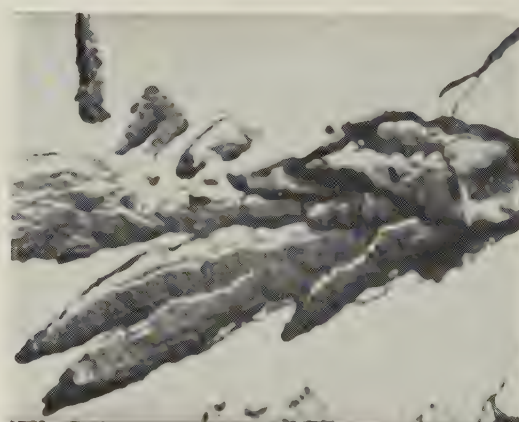
Fig. 5.



(1)

1 μ

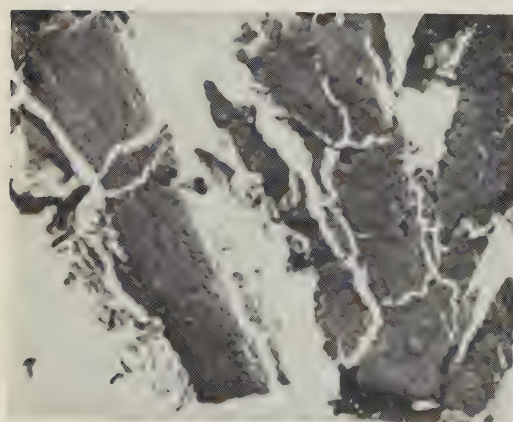
Fig. 4.



(2)

1 μ

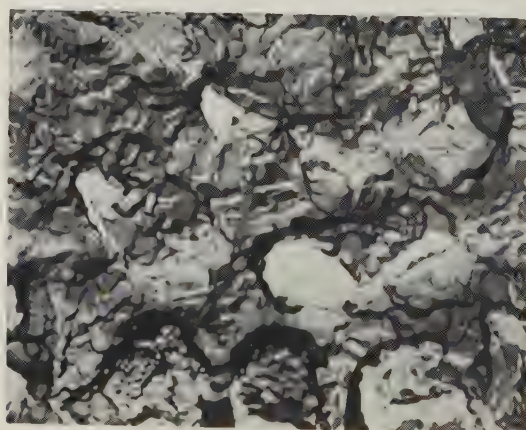
Fig. 5. 1,100°C 3 min.



(2)

1 μ

Fig. 4. 950°C 5 min.



1 μ

Fig. 6. 1,250°C 3 min.



Fig. 7. BaCO_3 before thermal decomposition.

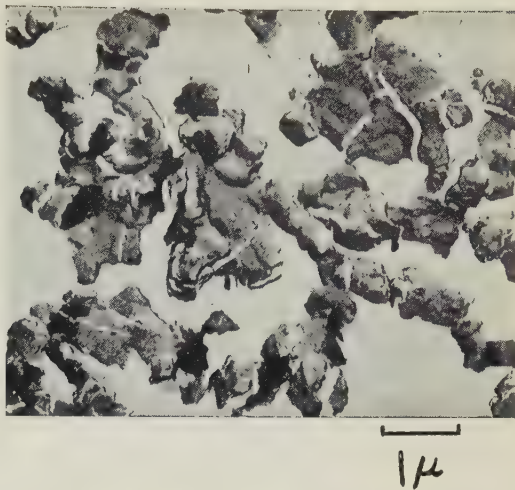


Fig. 10. 950°C 15 min.

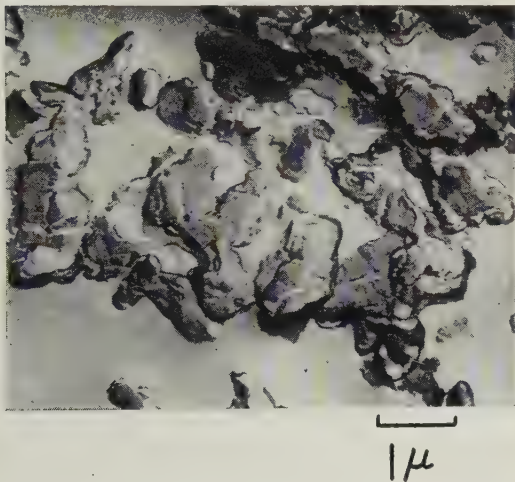


Fig. 8. Decomposition condition 700°C for 1hr., in vacuum.

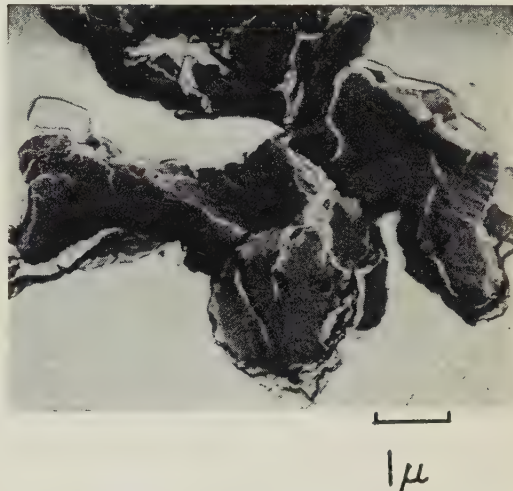


Fig. 11. 1100°C 8 min.

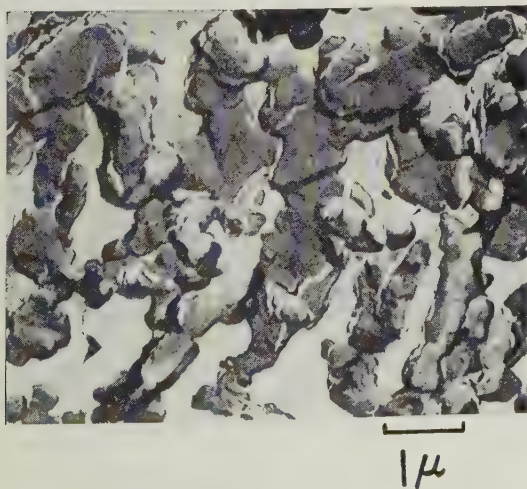


Fig. 9. 850°C 15 min.

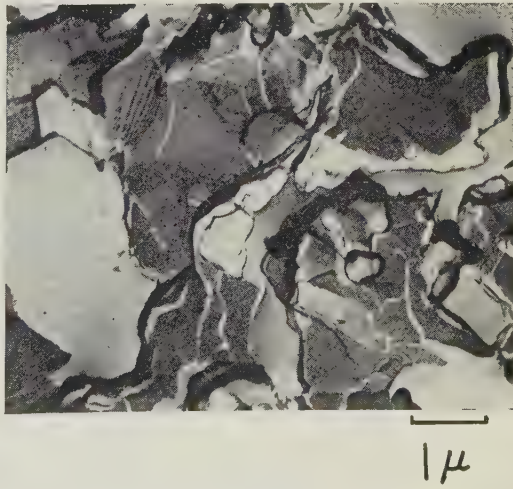


Fig. 12. 1.25°C 3 min.

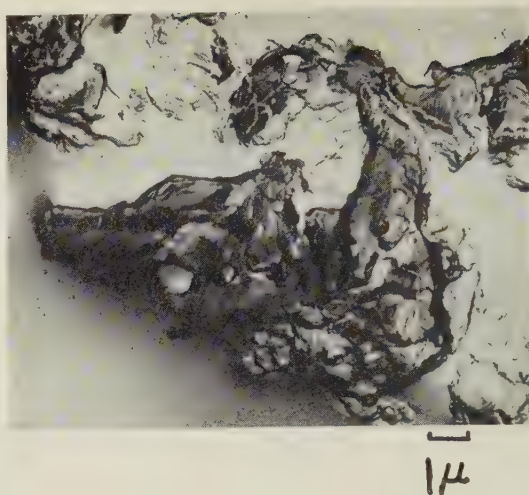
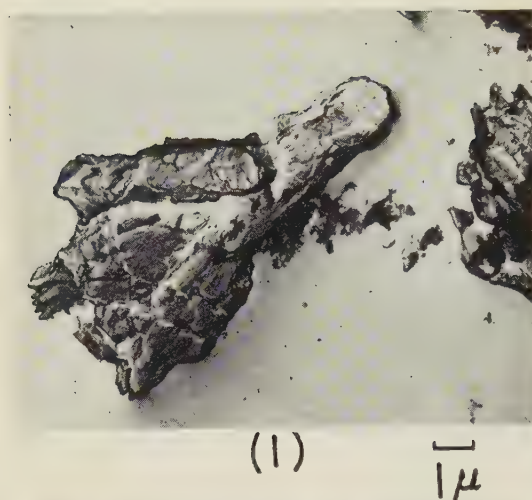


Fig. 14. Prolonged thermal treatment at 850°C for 5 hrs. after decomposition at 1,100°C for 3 min.

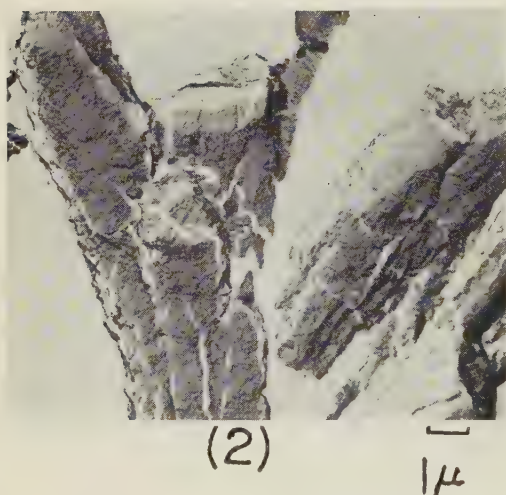


Fig. 13. Prolonged thermal treatment at 850°C for 5 hrs. is undertaken after decomposition at 850°C for 15 min.

of oxide particle reaches as large as 10 micron. Crystal growth of carbonate is also ascertained by the investigation of Wright³⁾ in which heat treatment is undertaken in the atmosphere of CO_2 for 30 min. In this case, crystal growth of carbonate begins at about 600°C and growth rate is especially larger for the carbonates which are coprecipitated with Na_2CO_3 .

Results similar to those of Eisentein have been obtained by X-ray diffraction study by Yamaka⁴⁾ for BaO, (BaSr)O and (BaSrCa)O. Crystal growth of (BaSr)O is enhanced abruptly at about 1050°C and the crystal size reaches 100Å at 1050°C, while it is 200~300Å at 900~1000°C. Aspects of this crystal growth, however, are little different for BaO and (BaSrCa)O. In the case of BaO, temperature

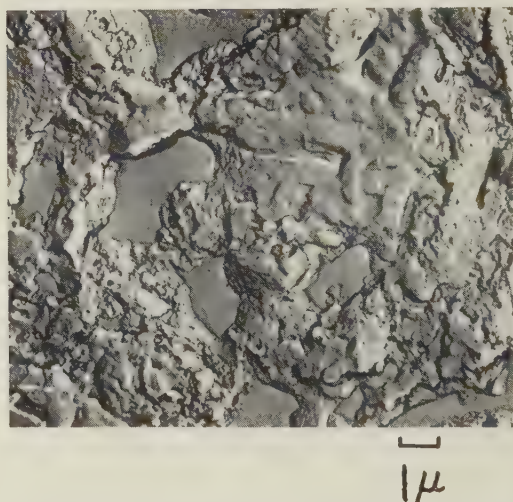


Fig. 16. The specimen decomposed thermally with same conditions as the of Fig. 6 but the specimen was exposed without formation of SiO replica.

at which abrupt crystal growth begins is lower than that for (BaSr)O by about 50°C, while in the case of (BaSrCa)O, crystal growth is less rapid. Another results have been given by Wright³⁾ which indicate that (BaSrCa)O, whose carbonate has been coprecipitated with NaCO_3 , has a crystal size of 0.5 micron at 900~1050°C. In his study, large difference is found in the growth rate of oxide crystal between specimens which are precipitated with various methods.

Considering these points, each result shown

above does not coincide very well with each other, but following common conclusions will be drawn from the studies by X-ray diffraction method. (1) Crystal growth of carbonate takes place at first before complete decomposition of carbonate to oxide. (2) Crystal growth of oxide becomes extensive above a certain critical temperature. For double and triple oxide, this critical temperature seems to exist around 1100°C . (3) For single oxide BaO, growth of oxide crystal is much easier than that for double and triple oxides. These three points which are deduced from X-ray analysis data may be applicable qualitatively to our present electron microscope observation. We can find in our photographs that growth of oxide crystals occurs markedly at a temperature between 1100°C and 1250°C in the case of decomposition process of triple carbonate. It is also clear from our observations that the crystal growth of single oxide begins at considerably lower temperature in comparison with that for the case of triple oxide. On the other hand, in considering the result (1), namely about the crystal growth of carbonate, it may be safely so stated. That larger grains, which are found on the surface of the specimen particle which is treated at 800°C (compare Fig. 3 with Fig. 4), will be attributed to the carbonate crystals which are grown considerably during the heat treatment.

Surface appearance of the specimen in Fig. 2 is not so different from that in Fig. 1. This implies that no significant change of carbonate crystal takes place during heat treatment at 700°C .

If we consider that a real crystal growth of oxide occurs at treating temperature above 900°C and if we also consider each fine particle on the specimen surface as a single crystal, we can estimate roughly the crystal size of the triple oxide as shown in Fig. 15 as a function of the decomposition temperature.

Considerable difference is found in the aspects of crystal growth between the single and the triple oxide. In the case of the single, each oxide particle consists originally of single crystal of about 0.5 micron and the crystal grows by a heat treatment at far lower temperature than for the triple. Each oxide particle is considered to consist of

polycrystals with many crystallites. When crystal grows, these many crystallites become centers of crystal growth. It may also be noted that, in the case of the single, melting of crystal is easily brought about when decomposition is made at high temperature. This will be reasonably ascribed to the formation of intermediate compound BaO. BaCO_3 which has a melting point as low as 900°C .

We can find the effect of prolonged heat treatment by comparison between Fig. 3 and Fig. 13. In Fig. 3, heating is done only for 15 minutes, while in Fig. 13, heat treatment

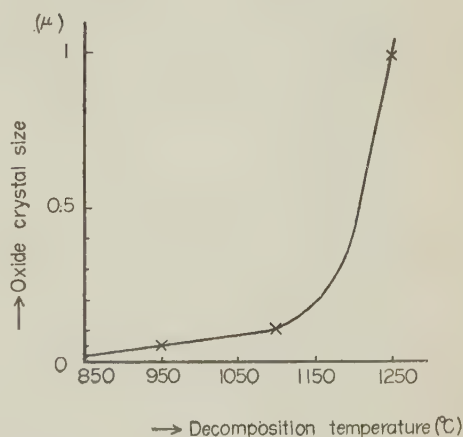


Fig. 15. Correlation between decomposition temperature and crystal size.

is continued for more than 5 hrs. It is considered, therefore, that in Fig. 3 the decomposition of carbonate does not finish, and in Fig. 13 not only the decomposition of carbonate is completed but the crystal of oxide has also grown up, owing to the prolonged heating at 850°C . A rough estimation gives an oxide crystal size of $200\sim 300\text{\AA}$ in Fig. 13. If we take this value as a crystal size at 850°C , this fits the curve in Fig. 15 showing the correlation between crystal size and treating temperature. It is interesting that appreciable difference is also found in the oxide crystal size between Fig. 5 and Fig. 14, in spite of the same condition of carbonate decomposition. This difference should be due to the fact that in Fig. 14 the continued heating after decomposition is imposed at 850°C for 5 hours, while in Fig. 5, only decompositions treatment is done.

Necessity of preparing of SiO film on the

specimen surface in high vacuum is clearly shown by the following experiment. Triple carbonates on both sides of flat nickel sleeve are decomposed at 1150°C (5 minutes heating), and deposition of SiO is made upon only one side of coating. Then, specimen is put out in the air and replica is prepared for the both sides of coating by the method mentioned in II B. Although the image similar to that shown in Fig. 6 obtained for the replica with SiO film, the one shown in Fig. 16 which is very different from Fig. 6 is obtained for the replica without SiO film. It may be clear that if the oxide coating after decomposition process is once taken out of the vacuum into the atmosphere, we could not obtain a replica which gives us a real image of oxide surface owing to the extreme transformations of it caused by chemical reaction between oxide and atmosphere.

§ 5. Conclusion

By means of a special replica technique, we can obtain a replica of the specimens which has a porous surface structure and which is very unstable in the atmosphere. This technique consists of SiO deposition in vacuum and of successive preparation of replica which is used for the powdered specimens. With this replica technique, the following results are obtained: (1) Growth of the oxide crystal becomes intense at a certain decomposition temperature. For triple carbonate, this critical temperature lies at around 1100°C. At lower temperatures, for instance at 700°C in the case of the triple, we could not find any appreciable change in the appearance of surface of the carbonate specimens. (2) For the single carbonate, crystal

growth of oxide occurs at considerably lower decomposition temperature than for the triple. (3) At the crystal growth of oxide, many fine crystallites appear on the surface of specimen particle in the case of the triple. In the case of single, one oxide particle grows up to the larger one as a whole. (4) In the case of triple coating, the effect of prolonged heating after decomposition process is studied that this heating makes the growth of oxide crystals appreciable.

The features of crystal growth of oxide coatings which are known only by the study with X-ray diffraction method are studied by the direct observation method, by the use of the electron microscope. Continued investigations are in progress concerning the relation between activity and crystal size of oxide coating.

The authors wish to express their hearty thanks to Mr. Noake for his useful discussions.

The authors also wish to thank Dr. Shindo and Dr. Kuwata for their encouragement during the course of this work.

References

- 1) A. Amakasu, M. Fukase, E. Sekine, M. Takahashi, H. Noake and S. Hirota: *Le Vide* N° **51** (1954) 43.
- 2) A. Eisenstein: *J. Appl. Phys.* **17** (1946) 434.
- 3) D. A. Wright: *Le Vide* N° **51** (1954) 58.
- 4) E. Yamaka: *J. Appl. Phys.* **23** (1952) 937.
- 5) H. R. Rooksby: *Brit. J. Appl. Phys.* **6** (1955) 272.
- 6) K. Yazawa, H. Yako and M. Kasahara: *To-shiba Rev.* **13** (1958) 1231.
- 7) S. Hirota: *Electron-Microscopy Japan* **6** (1958) 152.

Thermoluminescence of Zinc Sulfide Phosphors

By Kikusaburo OSADA

Faculty of Engineering, Nagoya University

(Received Sept. 4, 1959)

The glow curves of the thermoluminescence of some zinc sulfide phosphors are measured for two different exponential heating rates by means of an oscilloscope, and the values of the depth and frequency factor of their traps are obtained by the Booth method. The value of the frequency factor is not constant for all traps, but becomes larger as the depth increases.

The equations are also developed which permit the analysis of the glow curves for the exponential heating rate.

§1. Introduction

The thermoluminescence of the phosphors has been measured to obtain the origin and depth of the trapping centers. The correlation between the depth and the glow peak temperature were formulated by Randall and Wilkins¹⁾, and others²⁾. When the trap depth is calculated from these formulas, the value of the frequency factor is assumed to be equal to 10^8 sec^{-1} or the other reasonable numerical value for all traps. On the other hand, the value can be obtained from the measurements of the decay curves of the phosphorescence and the other phenomena. This value is not always in agreement with that assumed one.

So the other methods by which the frequency factor was explicitly obtained from the glow curve were developed by Garlick and Gibson³⁾, Grossweiner⁴⁾, and Booth⁵⁾. The first method is said to be inaccurate⁶⁾. When the second is used, the heating rate is restricted. By the last the values of the trap depth and frequency factor can be obtained without the assumption and the restriction.

The Booth method has been used for the analysis of the glow curves of a ZnS·Cl single crystal⁷⁾ and of a X-ray coloured KCl crystal⁸⁾, but not for the other zinc sulfide phosphors, although they have been measured by many workers.

Therefore, the glow curves of some zinc sulfide powdered phosphors were measured for two different exponential heating rates by means of an oscilloscope, and the values of the depth and frequency factor of the traps were calculated by the Booth method. And the observed values are compared with the ones which have been obtained from the

measurements of the other phenomena.

The equations are also developed which permit the analysis of the glow curves for the exponential heating rate.

§2. Preparation of Specimens

Zinc sulfide was precipitated by H_2S from aqueous solution of zinc sulfate which was one of commercial reagents of the special grade. The zinc sulfide was mixed with potassium chloride, or moreover one of lead acetate, manganese chloride, and cupric chloride, and was fired in air at about 950°C in an electric furnace. The initial concentrations of potassium chloride, lead acetate, manganese chloride, and cupric chloride were approximately 10%, 1%, 1%, and 0.1% in weight, respectively, but the final concentrations were unknown, as a part of them vaporized out probably during the firing. The zinc sulfide only was fired under the same condition.

When the phosphors are excited at room

Specimen	Fluores.	Phosphores.	$E(\text{eV})$	$s(\text{sec}^{-1})$
ZnS	yellow (very weak)	no	0.20	1.1×10^6
			0.42	4.5×10^7
ZnS·Cl	yellow	green	0.23	8.2×10^4
			0.43	7.5×10^7
ZnS·Mn·Cl	orange	orange	0.23	2.3×10^6
			0.36	5.9×10^6
			0.50	7.5×10^8
ZnS·Pb·Cl	yellow	green	0.33	7.8×10^7
			0.43	6.1×10^8
			0.58	2.5×10^{10}
ZnS·Cu·Cl	yellow	green	0.26	5.1×10^6
			0.56	1.3×10^{10}

Table I. Luminescence, trap depth, and frequency factor of the zinc sulfide phosphors.

temperature with the radiation of the black light lamp whose spectrum is a band in the range of $330\text{m}\mu\sim 380\text{m}\mu$ with a maximum at $355\text{m}\mu$, they emit the light as given in Table I. The ZnS phosphor phosphoresces also emitting a weak green light at low temperature.

§ 3. Analysis of Glow Curve

We shall calculate the shape of the glow curve, when the trap depth is single valued and when the temperature rises exponentially.

The rising of the temperature is given by

$$T = T_{\infty} - (T_{\infty} - T_0)\exp(-\alpha t), \quad (1)$$

where T is the absolute temperature at time t , T_{∞} the final one, T_0 the initial one, and α the decay constant.

Differentiating Eq. (1) with respect to t ,

$$dT = \alpha(T_{\infty} - T)dt. \quad (2)$$

By analogy with the derivation of the Randall and Wilkins formula¹⁾, the following equation is obtained:

$$I = C n_0 s \exp(-E/kT) \times \exp\left\{-\int_{T_0}^T \frac{s}{\alpha(T_{\infty} - T)} \exp(-E/kT) dT\right\}, \quad (3)$$

where I is the glow intensity, s the frequency factor, E the trap depth, k the Boltzmann constant, C a constant, and n_0 the initial number of the trapped electrons.

It is found from this equation that the glow curve has a single maximum. Differentiating Eq. (3) with respect to T and being equal to zero, the temperature at the glow maximum (T^*) is given by

$$\frac{E}{kT^{*2}} = \frac{s}{\alpha(T_{\infty} - T^*)} \exp(-E/kT^*). \quad (4)$$

The term $\alpha(T_{\infty} - T^*)$ is the heating rate at T^* .

If C , E , s , T_0 , T_{∞} , and α are assumed to be equal to unity, 0.3eV , 10^6 sec^{-1} , 150°K , 300°K , and $1/150\text{ sec}^{-1}$, respectively, a curve which has a maximum at 205°K is obtained by the numerical and graphical approximate calculation as shown in Fig. 1. The another curve for the constant heating rate is obtained as shown in the same figure, if the heating rate is 0.633 deg/sec for which the maximum of the curve is coincident with that of the former, and the others are equal to the previous values. The two curves are similar in

shape except that the former has the tail at the higher temperature side and its maximum value is larger than that of the latter.

When the heating rate decreases monotonously, it is also found that the glow curve has a single maximum and the maximum

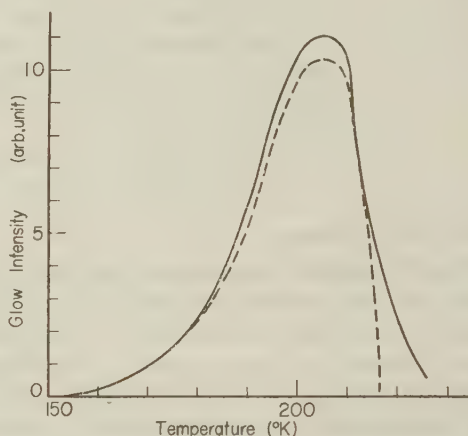


Fig. 1. Theoretical glow curves for the exponential (—) and the constant heating rates (----).

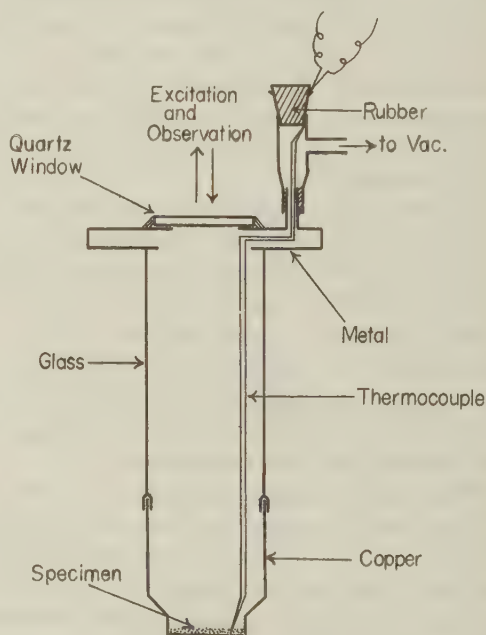


Fig. 2. Vessel for observation of thermoluminescence.

temperature is given by Eq. (4), in which the term $\alpha(T_{\infty} - T^*)$ is replaced with the heating rate (β) at T^* .

Measuring the glow curves for two different heating rates, the glow maximum temperature for each curve is given by

$$\frac{E}{kT_1^{*2}} = \frac{s}{\beta_1} \exp(-E/kT_1^*) \quad (5)$$

and

$$\frac{E}{kT_2^{*2}} = \frac{s}{\beta_2} \exp(-E/kT_2^*), \quad (6)$$

where the two curves for the different heating rates are indicated with suffixes 1 and 2.

The equations for the calculation of the trap depth and frequency factor are derived from Eqs. (5) and (6):

$$E = \left(\frac{kT_1^*T_2^*}{T_1^* - T_2^*} \right) \log \left(\frac{\beta_1 T_2^{*2}}{\beta_2 T_1^{*2}} \right) \quad (7)$$

and

$$s = \left(\frac{\beta_1 E}{kT_1^{*2}} \right) \exp(E/kT_1^*). \quad (8)$$

§ 4. Glow Curves

The specimen was set at the bottom of a vessel as shown in Fig. 2, cooled to -120°C by dipping the lower part into liquid air, and excited with the ultraviolet radiation of the black light lamp passed through the upper window. (As the experiment was carried out in vacuum, the lowest temperature attained was very high even by using liquid air. This result is in good agreement with that of Bube and Shrader.⁹⁾) Afterwards, when liquid air was taken out and the lower part was being maintained at room temperature, the specimen was warmed up exponentially as given by Eq. (1). So the glow of the specimen was observed through the upper window. The glow curve was recorded by means of an oscilloscope as shown in Fig. 3.¹⁰⁾ The temperature is detected with a copper-constantan thermocouple inserted in the specimen, and its electromotive force is fed to the horizontal deflectors of the cathode-ray tube. The glow is detected by a photo-multiplier tube (RCA 1P21), and its output is fed to the vertical deflectors. To know the heating rate, the time marks are displayed on the glow curve. The curves were obtained as shown in Fig. 4 and the heating rate was approximately 0.8 deg/sec and 0.2 deg/sec at 150°K and 250°K , respectively. To avoid the overlap of the curves in the figure, the intensity scale is arbitrary and independent for each curve. The results are similar to the ones obtained by Bube.¹¹⁾¹²⁾ All curves have two peaks and moreover the curves of the specimens containing lead or manganese have a shoulder at the higher temperature side. The glow intensity of the ZnS phosphor is

very weak and the second peak of ZnS·Cu·Cl is very intensive. The curves of ZnS·Cu·Cl which have been measured by many workers¹³⁾ are complicated, but the observed curve is simple because of the faster heating rate.

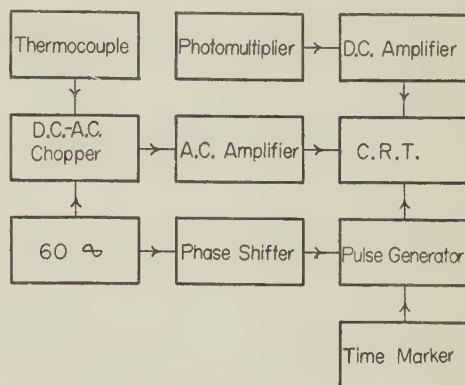


Fig. 3. Block diagram of apparatus for recording the glow curves.

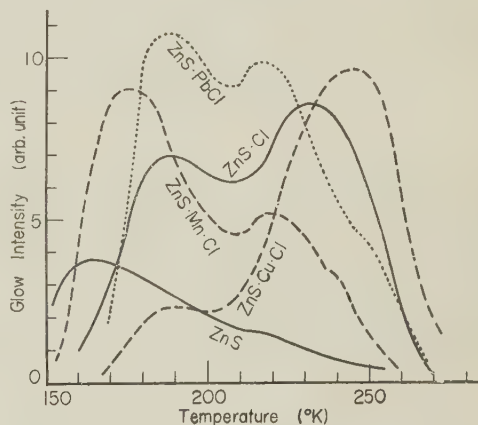


Fig. 4. Glow curves of the zinc sulfide phosphors.

When the lower part of the vessel was being maintained at about 50°C after liquid air was taken out, the heating rate was about five times faster. So all glow peaks and shoulders shifted about 20 degrees to the higher temperature side.

From the shift and the heating rate, the values of the trap depth and frequency factor are calculated by using Eqs. (7) and (8) as given in Table 1. The value of the frequency factor is found to increase with the depth.

§ 5. Discussion

The values of the frequency factor have been considered to be constant for all traps,

but the observed values are not constant. Here, we shall compare the observed values to the ones obtained from the other phenomena.

a) *ZnS·Cl*: The glow curves of the ZnS·Cl single crystal phosphor were analyzed by the Booth method, and the values of the depth and frequency factor of the traps due to chlorine ions were obtained to be 0.24 ± 0.02 eV and 7×10^4 sec⁻¹, whereas the *E*-value of the ZnS·Cl powdered phosphor was calculated to be 0.37 eV from the Randall and Wilkins formula assuming 10^8 sec⁻¹ as the *s*-value. Those values are discrepant.

On the other hand, the *s*-values for the traps of the CdS·Cl single crystal whose *E*-values were 0.35 eV and 0.63 eV were found to be 3×10^6 sec⁻¹ and 2×10^7 sec⁻¹, respectively, from the analysis of the curves of the thermally stimulated current by the Fermi-level or the Booth methods.¹⁴⁾

The former *s*-value for ZnS·Cl is of the same order of the magnitude as found for CdS·Cl. Therefore, the former values were reported to be more reasonable.⁷⁾ The observed values of the first peak are in satisfactory agreement with the formers. As the second peak does not appear on the glow curve of the ZnS·Cl single crystal, it seems to be due to oxygen. Its *s*-value is of the same order of the magnitude as found for the second trap of CdS·Cl.

b) *ZnS·Cu·Cl*. When the *E*-values of the traps have been obtained from the glow curves, the *s*-value has been assumed to be 10^8 sec⁻¹ or 10^{10} sec⁻¹. The *s*-values have been also measured from the other phenomena. From the decay curves of the phosphorescence, the *s*-values were obtained to be 3×10^{10} sec⁻¹ and 7×10^9 sec⁻¹ for the traps whose *E*-values were 1.0 eV and 0.89 eV, respectively.¹¹⁾ From the dielectric measurements, the values of the reciprocal of the relaxation time for electrons in traps which should be closely related to the *s*-values were found to be 6.3×10^6 sec⁻¹ and $2.5 \sim 1.3 \times 10^7$ sec⁻¹ for the ZnS·Cu and the ZnS·CdS·Cu phosphors, respectively.¹⁵⁾ But the *s*-values have not yet been derived from them.

The observed *s*-value for the second peak trap is of the same order of the magnitude as found from the decay curves.

c) *Others*: The *s*- and *E*-values for the Co-

trap of the ZnS·Cu·Co phosphor were found to be 5×10^4 sec⁻¹ and 0.51 eV from the analysis of the glow curve by the Garlick and Gibson method¹⁶⁾, but it was reported rather better to correct 0.68 eV as the *E*-value, assuming 10^8 sec⁻¹ as the *s*-value.⁶⁾ The another trap for which the *s*- and *E*-values were 1.3×10^{11} sec⁻¹ and 1.1 eV were also found from the decay curve of the phosphorescence.¹⁶⁾

The values for the ZnS·Cu·Mn phosphor were found to be 10^{11} sec⁻¹ and 1.0 eV.¹⁷⁾

From the above descriptions and the observed results, it may be concluded that the value of the frequency factor of the traps becomes larger as the depth increases. In other words, the electrons which are captured in the deeper trap couple more strongly with the crystal vibrations.

From the well-known relation¹⁸⁾ between the frequency of the escape from the trap and the capture cross-section(σ):

$$s/\sigma = 2(6)^{\frac{1}{2}} \pi^{\frac{1}{2}} m h^{-3} (kT)^2,$$

the capture cross-section of the trap is found to increase with the depth.

§ 6. Conclusion

The value of the frequency of escape from the traps of the zinc sulfide phosphors is not constant for all traps, but becomes larger as the depth increases.

References

- 1) J. T. Randall and M. H. F. Wilkins: Proc. Roy. Soc. **A184** (1945) 365.
- 2) G. R. Fonda and F. Seitz: *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley and Sons, New York, 1948) 87, 115. R. C. Herman and C. H. Meyer: J. Appl. Phys. **17** (1946) 743. F. E. Williams and H. Eyring: J. Chem. Phys. **15** (1947) 289.
- 3) G. F. J. Garlick and A. F. Gibson: Proc. Phys. Soc. London **60** (1948) 574.
- 4) L. I. Grossweiner: J. Appl. Phys. **24** (1953) 1306.
- 5) A. H. Booth: Canad. J. Chem. **32** (1954) 214.
- 6) C. H. Haake: J. Opt. Soc. Amer. **47** (1957) 649.
- 7) F. A. Kröger: Physica **22** (1956) 637.
- 8) A. Halperin and N. Kristianpollen: J. Opt. Soc. Amer. **48** (1958) 996.
- 9) R. H. Bube and R. E. Shrader: Rev. Sci. Instr. **25** (1954) 921.
- 10) K. Osada: Rev. Sci. Instr. **28** (1957) 1091.
- 11) R. H. Bube: Phys. Rev. **80** (1950) 655.
- 12) R. H. Bube: Phys. Rev. **90** (1953) 70.
- 13) A. W. Smith and J. Turkevich: Rhys. Pev. **87** (1952) 306. N. Riehl and H. Ortman: Z. Natur-

- forsch. **10a** (1955) 896. W. Reichardt and G. Tappe: Z. Naturforsch. **13a** (1958) 57.
- 14) R. H. Bube: J. Chem. Phys. **23** (1955) 18.
- 15) G. F. J. Garlick and A. F. Gibson: Proc. Roy. Soc. A, **188** (1947) 485.
- 16) W. Hoogenstraaten and H. A. Klasens: J. Electrochem. Soc. **100** (1953) 356.
- 17) W. Hoogenstraaten: J. Electrochem. Soc. **100** (1953) 356.
- 18) N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals* (Oxford Univ. Press, London, 1940) 108.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 1, JANUARY, 1960

A Refinement of the Linearized Transonic Flow Theory

By IWAO HOSOKAWA

*National Aeronautical Laboratory of Japan,
Shinkawa, Mitaka, Tokyo*

(Received August 14, 1959)

A new method is proposed to calculate the velocity and pressure distributions around a thin symmetrical aerofoil or a slender body of revolution flying at transonic speed. It is essentially a refinement of the linearized transonic flow theory due to Oswatitsch and Maeder, such that a correction term is introduced to take account of the nonlinear character of the transonic flow. As examples of application, a symmetrical circular-arc aerofoil and a circular-arc body of revolution in the sonic flow are dealt with, and the results are found to be in good agreement with experiments, except for the rear portion in the latter case.

§ 1. Introduction

As is well known, the flow around an obstacle in the nearly sonic free stream is governed by a nonlinear differential equation of mixed type. As a practical approximation method, the method of integral equation has been contrived by Oswatitsch and developed by Gullstrand and Spreiter^{1),2)}. But the method is only applicable to flows with free stream Mach number near critical, though it can account for the appearance of normal shock waves.

Oswatitsch³⁾ and Maeder⁴⁾ tried linearization of the transonic flow theory. Although this method seems to be very powerful, it has two unsatisfactory points; first the calculated flow is not influenced by the mixed-flow character that makes the essence of the transonic flow as Miles⁵⁾ has pointed out before, and secondly, according to Maeder's method of determining the value of the assumed constant K (see (2.2)), the movement of the sonic point on the aerofoil with increasing Mach number seems to be incorrectly

given at least for a circular-arc aerofoil, as is seen in Fig. 1.

In this paper, a refinement of the method is proposed to remove such defects and take account of the mixed-flow and nonlinear characters, by approximately calculating a correction term to the linearized transonic flow theory.

Recently, Spreiter^{6),7)} has put forward another simple and powerful method, called local linearization method. Our present method seems to give results which are comparable with those given by Spreiter's method (see Fig. 2 and 3), but ours is different from his in accounting for the occurrence of the transonic normal shock waves on the obstacle.

§ 2. Basic Equation

The basic equation for the transonic flow can be written in the form:

$$(1 - M_\infty^2)\Phi_{xx} + \Phi_{yy} + \Phi_{zz} = (\gamma + 1)M_\infty^2\Phi_x\Phi_{xx} \quad (2.1)$$

where $U_\infty\Phi$ is the perturbation velocity potential, U_∞ and M_∞ are the free stream velocity and Mach number respectively, γ is the ratio

of specific heats, and the x -axis is taken in the direction of the free stream. Maeder has approximated (2.1) by a linear equation:

thus giving a finite continuous solution

$$(1-M_\infty^2)\varphi_{xx}+\varphi_{yy}+\varphi_{zz}=K\varphi_x \tag{2.2}$$

$$\varphi=\varphi(x,y,z;K) \tag{2.3}$$

where K is a certain constant to be determined appropriately. This can be integrated subject to the usual linear boundary condition,

for each M_∞ .

Let us introduce a correction potential g defined as

$$\Phi=\varphi+g \tag{2.4}$$

Then we have, by (2.1)–(2.4),

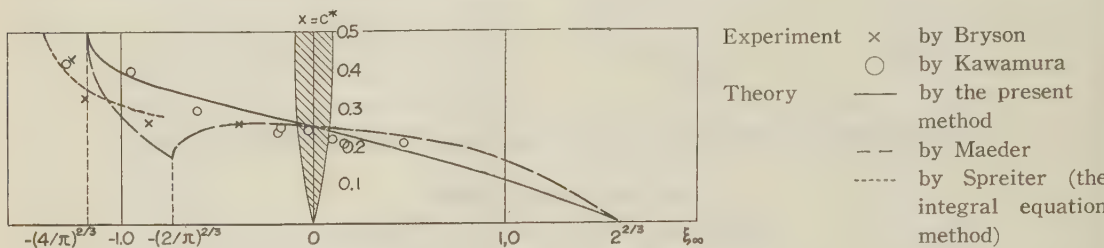


Fig. 1. Sonic point behaviour on the symmetrical circular-arc aerofoil with ξ_∞ .

$$g_{yy}+g_{zz}=\frac{\partial}{\partial x}\left[\{(M_\infty^2-1)+(\gamma+1)M_\infty^2\varphi_x\}g_x+\frac{1}{2}(\gamma+1)M_\infty^2g_x^2\right]+\{(\gamma+1)M_\infty^2\varphi_{xx}-K\}\varphi_x.$$

$$\tag{2.5}$$

The left-hand side of the equation is reduced to g_{yy} in the two-dimensional case, while it may be expressed as $g_{rr}+(1/r)g_r$ in the axisymmetric case where $r=(y^2+z^2)^{1/2}$. Also (2.5) shows the mixed-flow character such that it changes type according as

$$(M_\infty^2-1)+(\gamma+1)M_\infty^2\Phi_x\leqslant 0$$

$$\tag{2.6}$$

as should be expected. Here the equality holds for the sonic line or surface.

Now as a first step to find the solution g of (2.5) valid in the neighbourhood of the obstacle, let us consider the order of magnitude of various quantities in (2.5). According to Guderley⁸⁾, the both sides of (2.1) are considered to be of the same order $O(\tau^2)$. Here τ is defined as an expansion parameter such that

$$\Phi=O(\tau), \quad (\gamma+1)M_\infty^2\tau/(1-M_\infty^2)=O(1)$$

$$\tag{2.7}$$

and

$$x=L\bar{x}, \quad y=L\tau^{-1/2}\bar{y}, \quad z=L\tau^{-1/2}\bar{z} \tag{2.8}$$

where L is the length of the thin or slender obstacle, $\bar{x}$, $\bar{y}$ and $\bar{z}$ being $O(1)$. If t is the thickness ratio, it is related to τ as

$$\tau=O(t^{2/3}) \quad \text{or} \quad \tau=O(t^2)$$

$$\tag{2.9}$$

in the two-dimensional or axisymmetric case respectively.

Then the boundary condition of g on the obstacle will be that $g_y=O(\tau^{5/2})$, $g_z=O(\tau^{5/2})$ there, provided that φ has already been determined so as to satisfy the usual linear boundary condition. That is, if $U_\infty\Phi_x=u$ and $U_\infty\Phi_y=v$,

$$\frac{\Phi_y}{1+\Phi_x}\cong\varphi_y+g_y, \quad \frac{v}{U_\infty+u}=\frac{v}{U_\infty}-\frac{v}{U_\infty}\frac{u}{U_\infty}+\cdots$$

$$\varphi_y=\frac{v}{U_\infty}$$

and hence, with the aid of (2.7) and (2.8) we have

$$\left. \begin{aligned} g_y &= O\left(\frac{v}{U_\infty} \frac{u}{U_\infty}\right) = O(\tau^{3/2}\tau) = O(\tau^{5/2}) \\ \text{and similarly} \\ g_z &= O(\tau^{5/2}) \end{aligned} \right\} \quad (2.10)$$

except near the nose and tail of the obstacle. Therefore it is concluded that

$$g_{yy} + g_{zz} = O(\tau^3) \quad (2.11)$$

in the neighbourhood of the obstacle, while the right-hand side of (2.5) is generally considered as $O(\tau^2)$. Thus we may consider the left-hand side of (2.5) to be negligible in comparison with the right-hand side, at least near the obstacle. (For the axisymmetric case the estimation of order of magnitude should be performed in a slightly different manner. But the conclusion is the same as for the two-dimensional case.)

Now the basic equation can be simplified in the form:

$$\frac{\partial}{\partial x} \left[\{(M_\infty^2 - 1) + (\gamma + 1)M_\infty^2 \varphi_x\} g_x + \frac{1}{2} (\gamma + 1) M_\infty^2 g_x^2 \right] + \{(\gamma + 1)M_\infty^2 \varphi_{xx} - K\} \varphi_x = 0. \quad (2.12)$$

Further g is subjected to the condition, that it should vanish when the last inhomogeneous term in (2.5) or (2.12) vanishes identically. That is,

$$g \equiv 0, \quad \text{when } \{(\gamma + 1)M_\infty^2 \varphi_{xx} - K\} \varphi_x \equiv 0 \quad (2.13)$$

This means that Maeder's linearization is perfectly valid, or that there is no obstacle.

§ 3. Approximate Solution

The approximate equation (2.12) near the obstacle can be easily integrated to give

$$g_x = - \left\{ \varphi_x - \frac{1 - M_\infty^2}{(\gamma + 1)M_\infty^2} \right\} \pm \sqrt{\left\{ \varphi_x - \frac{1 - M_\infty^2}{(\gamma + 1)M_\infty^2} \right\}^2 - 2 \int_c^x \left\{ \varphi_{xx} - \frac{K}{(\gamma + 1)M_\infty^2} \right\} \varphi_x dx} \quad (3.1)$$

in which the double sign should be taken according as

$$\varphi_x - \frac{1 - M_\infty^2}{(\gamma + 1)M_\infty^2} \geq 0 \quad (3.2)$$

in order to satisfy the condition (2.13). It can readily be seen that g_x also satisfies the boundary condition at lateral infinity ($y \rightarrow \pm \infty$ or $r \rightarrow \infty$), since φ tends to zero there. The unknown constants c and K are uniquely determined in the following way.

First, g_x will in general be discontinuous at a point where

$$\varphi_x - \frac{1 - M_\infty^2}{(\gamma + 1)M_\infty^2} = 0, \quad (3.3)$$

But, from the physical point of view, any accelerating discontinuity of the flow velocity must be forbidden, so that we should have

$$g_x(c^*) = 0 \quad (3.4)$$

where $x = c^*$ is the point satisfying (3.3) in the accelerated flow region. This gives

$$c = c^* \quad (3.5)$$

Secondly, we know $\varphi_x(c^*) = \phi_x(c^*)$ from (2.4) and (3.4). With (2.6) and (3.3), this means that c^* is the sonic point and it is the same for the original linearized flow as for the corrected flow. This is in agreement with Oswatitsch's³⁾ inference that the linearized transonic flow field would be valid in the neighbourhood of the sonic point at least on the

obstacle. Therefore it may be expected that the best agreement of (2.1) and (2.2) would occur in the neighbourhood of $x=c^*$. Hence it is natural to take

$$K=(\gamma+1)M_\infty^2\varphi_{xx}(c^*)=(\gamma+1)M_\infty^2\varphi_{xx}(c^*) \quad (3.6)$$

Thus, the solution φ_x valid near the obstacle is completely determined as

$$\varphi_x = \frac{1-M_\infty^2}{(\gamma+1)M_\infty^2} \pm \sqrt{Y(x)} \quad (3.7)$$

where

$$Y(x) = \left\{ \varphi_x - \frac{1-M_\infty^2}{(\gamma+1)M_\infty^2} \right\}^2 - 2 \int_{c^*}^x \left\{ \varphi_{xx} - \frac{K}{(\gamma+1)M_\infty^2} \right\} \varphi_x dx \quad (3.8)$$

$$= \left\{ \frac{1-M_\infty^2}{(\gamma+1)M_\infty^2} \right\}^2 + \varphi_x^2(c^*) - 2 \frac{1-M_\infty^2}{(\gamma+1)M_\infty^2} \varphi_x(x) + 2 \frac{K}{(\gamma+1)M_\infty^2} \{ \varphi(x) - \varphi(c^*) \} \quad (3.9)$$

the double sign corresponding to $\varphi_x(x) \geq (1-M_\infty^2)/(\gamma+1)M_\infty^2$.

It is interesting to note that the proposal of (3.6) satisfies the two remarkable requirements. The one is that it can also assure the continuous connection with Prandtl-Glauert's theory at the critical Mach number as well as Maeder's proposal, since then we have $K=0$. The other is an essential analytical behaviour that the square root in (3.8) or (3.9) must not be imaginary.

Indeed we have, from (3.8),

$$dY/dx = 2\{ \varphi_{xx}(c^*)\varphi_x(x) - \varphi_x(c^*)\varphi_{xx}(x) \} \quad (3.10)$$

$$d^2Y/dx^2 = 2\{ \varphi_{xx}(c^*)\varphi_{xx}(x) - \varphi_x(c^*)\varphi_{xxx}(x) \} \quad (3.11)$$

with the aid of (3.3) and (3.6). Hence

$$Y(c^*)=0, \quad Y'(c^*)=0 \quad (3.12)$$

and

$$Y''(c^*) = 2\{ [\varphi_{xx}(c^*)]^2 - \varphi_x(c^*)\varphi_{xxx}(c^*) \} \quad (3.13)$$

But, if we confine ourselves to the transonic case such that $\varphi_x(c^*) \cong 0$, we should have $Y''(c^*) > 0$. From this and (3.12) we have

$$Y(x) \geq 0 \quad (3.14)$$

in the neighbourhood of the sonic point $x=c^*$. Further it seems to the author that the relation (3.14) will be generally valid for the main portion on the obstacle. But, in case it breaks down, for example in the neighbourhood of the nose and tail of the body of revolution in the supersonic flow, φ_x as given by the linearized transonic flow theory will give a rather good approximation there.

§ 4. Physical Implications

1) Sonic Point Behaviour

In the present method, the sonic point c^* is determined simultaneously with K by the equations:

$$\frac{1-M_\infty^2}{(\gamma+1)M_\infty^2} = \varphi_x(c^*; K) \quad (4.1)$$

$$\frac{K}{(\gamma+1)M_\infty^2} = \varphi_{xx}(c^*; K). \quad (4.2)$$

Above the free stream critical Mach number, $K \geq 0$ and c^* moves monotonously forward with increasing Mach number.

In the present approximation, freezing of the flow field at $M_\infty=1$ cannot be accounted for, though the sonic point behaviour with increasing M_∞ for the entire transonic range is qualitatively more reasonably given by this than by any other one single approximation method. In Fig. 1, the sonic point behaviour of a symmetrical circular-arc aerofoil is shown and is compared with the results by Maeder^{*}) and Spreiter²⁾ (the integral equation method) and with experiments by Bryson⁹⁾ and Kawamura¹⁰⁾.

2) Transonic Normal Shock Wave

In some cases, (3.3) has another root c^{**} which is in the decelerated flow region. Then, as is known from (3.7), the flow velocity has a finite discontinuous jump of equal amount $\sqrt{Y(c^{**})}$ from the sonic velocity at the point $x=c^{**}$ which may be quantitatively interpreted as a transonic normal shock wave. Appearance of such an irregular point is due to the quadratic behaviour of g_x in (2.12) and hence in (2.5) as well as in the case of the integral equation method.

It appears usually in the supercritical flow, but arrives at the trailing edge when $M_\infty=1$ in the two-dimensional biconvex case, as is assured by investigating the behaviour of φ_x .

3) Limiting Form of Φ_x

We have so far considered the transonic case such that the root of (3.3) exists. But it is also possible to predict the asymptotic approach to the sub- or supersonic linear theory as M_∞ tends to zero or infinity.

In order to achieve the continuity of our transonic solution to the sub- and supersonic solutions through the lower and upper critical Mach numbers respectively, we adopt the following prescriptions to determine the values of c and K , when the real root of (3.3) does not exist. For the subsonic case, (either two-dimensional or axisymmetric), c is taken to be the critical value c^* corresponding to the lower critical Mach number, which corresponds to the point of maximum flow velocity for the incompressible flow. On the other hand, for the two-dimensional supersonic case, we take $c \equiv c^*=0$, that means the leading edge. (It is not necessary to consider the axisymmetric supersonic case.) And hence K is uniquely given by (3.6).

With these extended definitions, the limiting form of Φ_x is obtained as

$$\Phi_x = \varphi_x(x) + \frac{(\gamma+1)M_\infty^2}{2(1-M_\infty^2)} \{\varphi_x^2(x) - \varphi_x^2(c^*)\} - \frac{K}{1-M_\infty^2} \{\varphi(x) - \varphi(c^*)\} \quad (4.3)$$

since the last term in (3.9) tends to zero as $M_\infty \rightarrow 0$ or ∞ , and

$$\frac{|M_\infty^2 - 1|}{(\gamma+1)M_\infty^2} \gg |\varphi_x| \quad (4.4)$$

in the sense of small perturbation. Of course φ itself tends to the conventional sub- or supersonic linear potential.

In consequence, the final formula (3.7) is still valid throughout the whole Mach number range.

§ 5. Examples of Sonic Flow ($M_\infty=1$)

In the case of the sonic flow, Maeder's formal solution for φ can be expressed in the following simple form, on and near the obstacle.

For the two-dimensional flow past a thin symmetrical aerofoil:

^{*}) This result was calculated by the author according to Maeder's theory (by use of (A1) and (A2)). Then it is remarkable that in the flow with ξ_∞ below $-(2/\pi)^{2/3}$, K vanishes so that there is no drag, while in the present method K does not vanish for ξ_∞ over the critical value, $-(4/\pi)^{2/3}$. The detailed explanation about the reason will be performed in the author's later paper. Here ξ_∞ is a transonic similarity parameter, $(M_\infty^2 - 1)/[(\gamma+1)tM_\infty^2]^{2/3}$, defined by Spreiter.

$$\varphi(x, y) = -\frac{1}{\sqrt{\pi K}} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} F^{(n+1)}(x) \frac{x^{n+(1/2)}}{2n+1} + \frac{1}{2} |y| F'(x) + O(t^3), \quad 0 < x < 1 \quad (5.1)$$

For the axisymmetric flow past a slender body of revolution:

$$\varphi(x, r) = \frac{1}{4\pi} F'(x) \log \frac{e^C K r^2}{4x} - \frac{1}{4\pi} \sum_{n=1}^{\infty} F^{(n+1)}(x) \frac{(-1)^n}{n \cdot n!} x^n + O(t^4 \log t), \quad 0 < x < 1 \quad (5.2)$$

where $F(x)$ is the cross-sectional area of the obstacle whose length is $L=1$, and C is Euler's constant. (see Appendix.)

A circular-arc aerofoil of thickness t is approximately given by $|y|=s(x)=2t(x-x^2)$, $0 \leq x \leq 1$, and hence

$$F(x) = 2s(x) = 4t(x-x^2), \quad 0 \leq x \leq 1 \quad (5.3)$$

Similarly, for the circular-arc body of revolution we have

$$F(x) = \pi s^2(x) = 4\pi t^2(x-x^2)^2, \quad 0 \leq x \leq 1 \quad (5.4)$$

Calculating Φ_x straightforwardly by the prescribed method, and using the usual approximate expression for the pressure coefficient C_p , we can obtain the distributions of C_p on the above

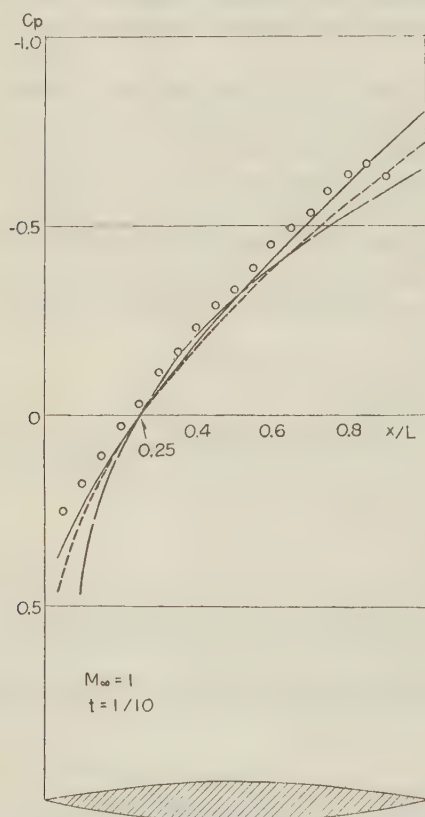


Fig. 2. C_p -distribution on a symmetrical circular arc aerofoil.

Experiment	○	by Michel, Marchaud and Le Gallo
Theory	—	by the present method
	- -	by Maeder
		by Spreiter (the local linearization method)

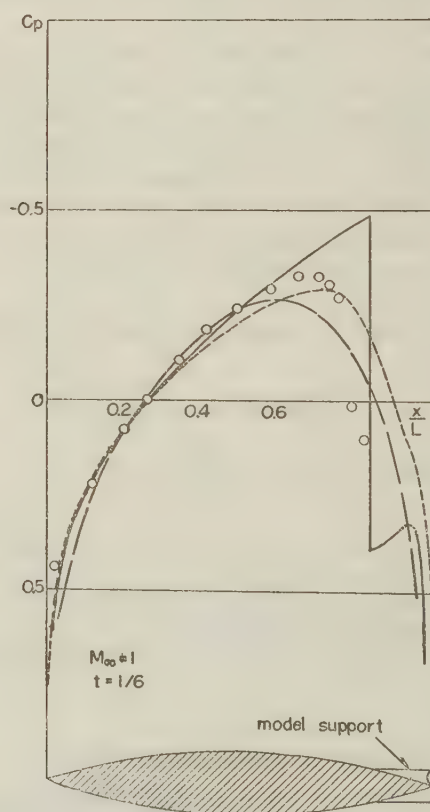


Fig. 3. C_p -distribution on a circular-arc body of revolution.

Experiment	○	by Drougge
Theory	—	by the present method
	- -	by Maeder
		by Spreiter (the local linearization method)

described obstacles of $t=0.1$ and $t=1/6$ respectively, as in Figs. 2 and 3. It will be seen that the present results are the most satisfactory among the various theoretical results, in view of the agreement with the experimental ones by Michel, Marchaud and Le Gallo⁽¹¹⁾ and Drougge⁽¹²⁾. In Fig. 3, the curve has been corrected near the nose and tail, taking account of the fact described in § 3.*

It is noted in particular that a transonic normal shock wave stays on the axisymmetric body and its nose and tail are the stagnation points. But as viscous effects destroy such a shock wave on the obstacle, any quantitative discussion about it seems to be without physical significance.

§ 6. Conclusion

The present method is essentially a refinement of the linearized transonic flow theory, such that the nonlinear characteristics of the fundamental equation is taken into account and the unambiguous determination of the value of K can be made. Also it has an advantage over the integral equation method in simplicity and applicability and over Spreiter's local linearization method in covering the two-dimensional high subsonic flow with a normal shock wave standing on the obstacle as well.

Since our method starts from the linearized transonic flow equation, any solution can be constructed by superposition even in the lifting case, although the final velocity ϕ_x for a definite K is no longer superposable. Therefore this method is expected to be the most practical of the existing approximate methods for the transonic flow.

Acknowledgements

The author wishes to express his sincere gratitude to Professor I. Imai, his co-researchers and to Professor R. Kawamura for their valuable discussions and continual encouragements. He is also deeply indebted to Dr. M. Yamanouchi, Mr. T. Shigemi and Mr. T. Murasaki for their kind support given to this study at the National Aeronautical Laboratory of Japan.

The author is particularly grateful to Dr. John R. Spreiter of Ames Research Center, N. A. S. A., for his encouragement and instructive comments upon this work.

Appendix

The original linearized transonic potentials corresponding to (2.3) are

$$\varphi(x, y) = -\frac{1}{2\pi} \int_0^1 F'(\xi) e^{\alpha(x-\xi)} \frac{K_0[\alpha\{(x-\xi)^2 + \beta^2 y^2\}^{1/2}]}{\beta} d\xi, \quad M_\infty \leq 1 \quad (A1)$$

$$= -\frac{1}{2} \int_0^{x-m|y|} F'(\xi) e^{\alpha(x-\xi)} \frac{I_0[\alpha\{(x-\xi)^2 - m^2 y^2\}^{1/2}]}{m} d\xi, \quad M_\infty \geq 1 \quad (A2)**$$

and

$$\varphi(x, r) = -\frac{1}{4\pi} \int_0^1 F'(\xi) e^{\alpha(x-\xi)} \frac{\exp[-\alpha\{(x-\xi)^2 + \beta^2 r^2\}^{1/2}]}{\{(x-\xi)^2 + \beta^2 r^2\}^{1/2}} d\xi, \quad M_\infty \leq 1 \quad (A3)$$

$$= -\frac{1}{2\pi} \int_0^{x-mr} F'(\xi) e^{\alpha(x-\xi)} \frac{\cosh[\alpha\{(x-\xi)^2 - m^2 r^2\}^{1/2}]}{\{(x-\xi)^2 - m^2 r^2\}^{1/2}} d\xi, \quad M_\infty \geq 1 \quad (A4)$$

* The details of the correction are as follows: the proposed method is applied without any modification to the main portion of the body ($x=0.15 \sim 0.9$) and the pressure distribution there, which contributes mostly to the total drag, is calculated with the aid of the usual expression of C_p for the axisymmetric body in the small perturbation theory; while in the vicinity of the nose and the tail, where the method is anticipated to fail gradually, φ_x itself is employed in place of ϕ_x because the former is considered to be more reasonable in the analytical behaviour than the latter, which does not necessarily tend to real minus infinity as should be expected in the axisymmetric case from the viewpoint of the linearized theory. The continuation of the C_p -curve at the front part of the body is very good; but at the rear part it does not seem to be so smooth, so that interpolation of some kind for rounding off a sharp corner at the point of connection has to be made.

** The expression (A2) is somewhat different from Maeder's one, but the latter is not correct.

where K_0 and I_0 are the modified Bessel functions of the zeroth order, and α , β and m are connected with one another as follows,

$$\alpha = \frac{K}{2\beta^2} = -\frac{K}{2m^2}, \quad \beta^2 = 1 - M_\infty^2 = -m^2 \quad (\text{A5})$$

These potentials can be integrated out on and near the obstacle as follows.

(1) The expressions (A1) and (A2) tend to

$$\varphi(x, y) = -\frac{1}{2\sqrt{\pi}K} \int_0^x F'(x) \frac{\exp[-Ky^2/4(x-\xi)]}{\sqrt{x-\xi}} d\xi \quad (\text{A6})$$

as $M_\infty \rightarrow 1 \pm 0$. With the substitution,

$$\frac{Ky^2}{4(x-\xi)} = u^2, \quad \frac{d\xi}{x-\xi} = 2 \frac{du}{u} \quad (\text{A7})$$

and by the Taylor expansion of $F'(x - Ky^2/4u^2)$,

$$\varphi(x, y) = -\frac{|y|}{2\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} F^{(n+1)}(x) \left(\frac{Ky^2}{4}\right)^n \int_{(Ky^2/4x)^{1/2}}^{\infty} \frac{e^{-u^2}}{u^{2(n+1)}} du, \quad 0 < x < 1 \quad (\text{A8})$$

Integrations in (A8) can be much simplified by the recurrence relation,

$$J_{n+1} = \frac{2^{2(n+1)}(n+1)!}{\{2(n+1)\}!} \left\{ \sum_{k=0}^n (-1)^k \frac{\{2(n-k)\}!}{(n-k)! 2^{2(n-k)+1}} \frac{\exp(-Ky^2/4x)}{(Ky^2/4x)^{n-k+(1/2)}} + (-1)^{n+1} J_0 \right\} \quad (\text{A9})$$

where

$$J_n = \int_{(Ky^2/4x)^{1/2}}^{\infty} \frac{e^{-u^2}}{u^{2n}} du, \quad n \geq 0 \quad \text{and} \quad J_0 = \frac{\sqrt{\pi}}{2} + O(|y|). \quad (\text{A10})$$

The linear term with respect to $|y|$ in J_0 does not influence that in the following formula (A11). Thus,

$$\varphi(x, y) = -\frac{1}{\sqrt{\pi}K} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} F^{(n+1)}(x) \frac{x^{n+(1/2)}}{2n+1} + \frac{1}{2} |y| F'(x) + O(y^3), \quad 0 < x < 1 \quad (\text{A11})$$

(2) The expressions (A3) and (A4) tend to

$$\varphi(x, r) = -\frac{1}{4\pi} \int_0^x F'(\xi) \frac{\exp[-Kr^2/4(x-\xi)]}{x-\xi} d\xi \quad (\text{A12})$$

as $M_\infty \rightarrow 1 \pm 0$. With the substitution similar to the previous case,

$$\frac{Kr^2}{4(x-\xi)} = u, \quad \frac{d\xi}{x-\xi} = \frac{du}{u} \quad (\text{A13})$$

and by the Taylor expansion of $F'(x - Kr^2/4u)$,

$$\varphi(x, r) = -\frac{1}{4\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} F^{(n+1)}(x) \left(\frac{Kr^2}{4}\right)^n \int_{Kr^2/4x}^{\infty} \frac{e^{-u}}{u^{n+1}} du, \quad 0 < x < 1. \quad (\text{A14})$$

The recurrence formula is in this case

$$J_{n+1} = \frac{1}{n!} \left[\sum_{k=0}^{n-1} (-1)^k (n-k-1)! \frac{\exp(-Kr^2/4x)}{(Kr^2/4x)^{n-k}} + (-1)^n J_1 \right], \quad n \geq 1 \quad (\text{A15})$$

where

$$J_n = \int_{Kr^2/4x}^{\infty} \frac{e^{-u}}{u^n} du$$

and

$$J_1 = \text{Ei} \left(\frac{Kr^2}{4x} \right) = -C - \log \frac{Kr^2}{4x} + \frac{Kr^2}{4x} + O \left\{ \left(\frac{Kr^2}{4x} \right)^2 \log \frac{Kr^2}{4x} \right\} \quad \left. \vphantom{\int_{Kr^2/4x}^{\infty}} \right\} \quad (\text{A16})$$

Consequently,

$$\varphi(x, r) = \frac{1}{4\pi} F'(x) \log \frac{e^C Kr^2}{4x} - \frac{1}{4\pi} \sum_{n=1} F^{(n+1)}(x) \frac{(-1)^n}{n \cdot n!} x^n + O(t^4 \log t), \quad 0 < x < 1. \quad (\text{A17})$$

It is obvious that the both expressions (A11) and (A17) satisfy the linear boundary conditions on the obstacles.

References

- 1) J. R. Spreiter and A. Y. Alksne: NACA Tech. Rep. 1217 (1955).
- 2) J. R. Spreiter and A. Y. Alksne: NACA Tech. Note 4148 (1958).
- 3) K. Oswatitsch and F. Keune: Proc. Conf. on High Speed Aeronautics, Polytech. Inst. Brooklyn (1955).
- 4) P. F. Maeder and H. U. Thommen: J. Aero. Sci. **23** (1956) 187.
- 5) J. W. Miles: J. Aero. Sci. **23** (1956) 704.
- 6) J. R. Spreiter and A. Y. Alksne: NACA Tech. Rep. 1359 (1958).
- 7) J. R. Spreiter and A. Y. Alksne: NASA Rep. 2 (1959).
- 8) K. G. Guderley: *Theorie Schallnaher Strömungen* (Springer, 1957) 33.
- 9) A. E. Bryson: NACA Tech. Rep. 1094 (1952).
- 10) R. Kawamura and K. Karashima: Read at the 13th Annual Meeting of Phys. Soc. Japan, Oct. 1958.
- 11) R. Michel, F. Marchaud and J. Le Gallo: ONERA, Publication no. 65 (1953).
- 12) G. Drougge: Proc. 9th Intern. Congr. Appl. Mech., vol. 2 (1957) 70.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 1, JANUARY, 1960

General Theory of Electrically Conducting Perfect Gas Flow past a Three-Dimensional Thin Body

By Shigenori ANDO

Engineering Div., Gifu Seisakusho, Kawasaki Aircraft Co.

(Received August 22, 1959)

General theory of electrically conducting gas past a three-dimensional thin body is presented. Fundamental equation for a parametric function is derived. The magnetic field, the flow velocity and the pressure are all connected to the parametric function, and so the boundary conditions for the fundamental equation can be written explicitly. The flow over a wavy wall is treated as an application of the present theory in which the applied magnetic field may be in an arbitrary direction.

§ 1. Introduction

Small disturbance method introduced into magneto-hydrodynamics by Sears and Resler¹⁾ is a very attractive, because this method may bring about some extensive systems of theory and many instructive physical images as in

conventional gas dynamics.

Small disturbance theory in general deals with inviscid and, in most cases, steady flow. It takes one of various different forms in accordance with the assumptions for compressibility of the fluid, for electric conductivity

or magnetic Reynolds number of the flow, for direction of the applied magnetic field and for the spatial extension of the body in study (that is, either two- or three-dimensional).

Sears and Resler¹⁾ calculated several interesting examples under the assumptions that the magnetic Reynolds number is infinity, that the applied magnetic field is parallel or normal to the free stream, that the fluid is incompressible and that the flow is two-dimensional. According to Sears' lecture²⁾, their investigations were extended to the flow with finite magnetic Reynolds number and with compressibility, but the applied field was still parallel or normal to the free stream. In these investigations attention was given to some particular problems, and no general theory of small perturbation was presented. Sakurai³⁾ presented a general theory of perfect gas past a two-dimensional thin body under the assumptions that the direction of applied field and magnetic Reynolds number are both arbitrary. He derived a "fundamental equation" (partial differential equation) for a "parametric function" (generalized stream function). However, he neither used it to solve practical problems nor showed the equations relating magnetic field to his parametric function. All the above mentioned investigations were restricted to the two-dimensional flow.

In the present paper is derived a general fundamental equation for the steady flow of inviscid perfect gas past a three-dimensional thin body. The magnetic Reynolds number and the direction of applied field may be arbitrary. The fundamental equation is written for a parametric function to which the magnetic field, the flow velocity and the pressure are all connected in compact and reasonable forms. In the case of two-dimensional flow, this fundamental equation has the same form as that derived by Sakurai³⁾, but the present parametric function is connected not only to the flow velocity but also to the magnetic field. Therefore boundary conditions can be expressed in terms of this function when necessary, and so the mathematical

formulation of the problem may be completed. Once general fundamental equation is derived, it is easy to get the fundamental equations for the special cases treated by the previous writers, Resler, Sears, and Sakurai.

As an application of the general theory the flow over a wavy wall is treated in case when the magnetic field is applied in an arbitrary direction. This problem is interesting because the two extreme cases with parallel and normal magnetic fields, calculated by Sears and Resler¹⁾, are of entirely different character.

A reduction of the general theory also shows an interesting phenomenon that the perturbation wave may travel obliquely forward when Alfvén number is less than unity.

§ 2. General Theory

2.1 Non-dimensionalized basic equations

Suppose that a three-dimensional thin body flies with constant velocity in a inviscid perfect gas with electrical conductivity. It is assumed that the conventional magnetohydrodynamic approximations are valid. As the electromagnetic unit, MKS rationalized system is used.

The basic (starting) equations are written in the conventional notations referring to the frame fixed to the flying body as follows;

$$\text{rot } \mathbf{E}_* = 0 \quad (1)$$

$$\text{div } \mathbf{E}_* = \rho e_* \quad (2)$$

$$\text{rot } \mathbf{B}_* = R_m \mathbf{J}_* \quad (3)$$

$$\text{div } \mathbf{B}_* = 0 \quad (4)$$

$$\mathbf{J}_* = \mathbf{E}_* + \mathbf{q}_* \times \mathbf{B}_* \quad (5)$$

$$\text{div } (\rho_* \mathbf{q}_*) = 0 \quad (6)$$

$$\rho_* (\mathbf{q}_* \cdot \nabla) \mathbf{q}_* = -\text{grad } p_* + R_m S (\mathbf{J}_* \times \mathbf{B}_*) \quad (7)$$

$$(\gamma - 1)^{-1} \rho_* (\mathbf{q}_* \cdot \nabla) T_* = -p_* \text{div } \mathbf{q}_* + R_m S \mathbf{J}_*^2 \quad (8)$$

$$p_* = \rho_* T_* \quad (9)$$

(1), (2), (3) and (4) are Maxwell's Eqs. (5) is Ohm's law, (6) is continuity Eq. (7) is momentum Eq. (8) is energy Eq. and (9) is Eq. of state of perfect gas. The quantities marked with asterisk are non-dimensional and defined in the following ways;

$$\mathbf{q}_* = \bar{\mathbf{q}} / \bar{u}_\infty \quad ; \quad \text{Flow velocity, vector.}$$

$$\rho_* = \bar{\rho} / \bar{\rho}_\infty \quad ; \quad \text{Density.}$$

$$p_* = \bar{p} / \bar{\rho}_\infty \bar{u}_\infty^2 \quad ; \quad \text{Pressure.}$$

$$\begin{aligned}
T_* &= R\bar{T} / \bar{u}_\infty^2 && ; \text{ Temperature.} \\
B_* &= \bar{B} / \bar{B}_\infty && ; \text{ Magnetic flux density, vector.} \\
E_* &= \bar{E} / \bar{u}_\infty \bar{B}_\infty && ; \text{ Electric field, vector.} \\
J_* &= \bar{J} / \sigma \bar{u}_\infty \bar{B}_\infty && ; \text{ Current density, vector.} \\
\left. \begin{aligned} x &= \bar{x} / L \\ y &= \bar{y} / L \\ z &= \bar{z} / L \end{aligned} \right\} && \text{Coordinates. The unit vector in the } x\text{-direction is} \\ && ; \text{ denoted as } i. \text{ Free stream direction is chosen as the} \\ && \text{ } x\text{-axis.} \\
R_m &= \mu_e \sigma L \bar{u}_\infty && ; \text{ Magnetic Reynolds number.} \\
S &\equiv \bar{B}_\infty^2 / \mu_e \bar{\rho}_\infty \bar{u}_\infty^2 \equiv N^{-2} && ; \text{ Pressure number.} \\
N &&& ; \text{ Alfvén number.}
\end{aligned}$$

The quantities marked with bar represent the original ones having dimensions. Subscript "∞" represents free stream condition.

As it is very inconvenient to use all equations from (1) to (9), all the quantities except q_* and B_* are eliminated. First, J_* and E_* are eliminated as follows. From (1), (3) and (5), the so-called induction equation is derived,

$$R_m \operatorname{rot} (q_* \times B_*) + \nabla^2 B_* = 0 \quad (10)$$

The momentum Eq. (7) is reduced to the form

$$\rho_* (q_* \cdot \nabla) q_* = -\nabla p_* + S (\operatorname{rot} B_*) \times B_* \quad (11)$$

The energy Eq. (8) is reduced to

$$(\gamma - 1)^{-1} \rho_* (q_* \cdot \nabla) T_* = -p_* \operatorname{div} q_* + (S/R_m) (\operatorname{rot} B_*)^2 \quad (12)$$

ρ_* , p_* and T_* in the above equations will be eliminated in the next section.

2.2 Linearization of the basic equations

First we take the frame (S') fixed to the free stream, and suppose that a thin body flies towards the direction $x' = -\infty$. Assume that in this frame the magnetic field is uniform, $\bar{B}_\infty'(\bar{B}'_{\infty z}, \bar{B}'_{\infty y}, 0)$, the electric field is $\bar{E}_\infty'(0, 0, 0)$ and the current density is $\bar{J}_\infty'(0, 0, 0)$. Then Lorentz transformation from this frame (S') to the frame (S) fixed to the flying body shows that

$$\begin{aligned}
&\text{electric field w.r.t. (S),} && \bar{E}_\infty = (-\bar{q}_\infty) \times \bar{B}_\infty' \\
&\text{magnetic flux density w.r.t. (S),} && \bar{B}_\infty = \bar{B}_\infty'
\end{aligned}$$

Therefore $E_*(x = -\infty) \equiv E_\infty = -i \times B_\infty$, and current density at infinity w.r.t. (S), $J_\infty = E_\infty + i \times B_\infty = 0$. After this we use the frame (S) only.

Non-dimensional quantities marked with asterisk may be divided into two parts. The ones are the unperturbed quantities and the others are the perturbed quantities. It is assumed that the latter are very small and their second and higher order small quantities are negligible.

$$\left. \begin{aligned}
q_* &= (i + v), && v(u, v, w) \\
B_* &= B_\infty + b, && B_\infty(\cos \theta, \sin \theta, 0), \quad b(b_x, b_y, b_z) \\
p_* &= p_\infty + p \\
\rho_* &= \rho_\infty + \rho = 1 + \rho \\
T_* &= T_\infty + T \\
E_* &= -i \times B_\infty + E, && E(E_x, E_y, E_z) \\
J_* &= 0 + j, && j(j_x, j_y, j_z) \\
u, v, w; &b_x, b_y, b_z; && p, \rho, T; E_x, E_y, E_z; j_x, j_y, j_z \ll 1.
\end{aligned} \right\} \quad (13)$$

Then, induction Eq. (10) is linearized as follows;

$$R_m \left\{ -\frac{\partial \mathbf{b}}{\partial x} + (\mathbf{B}_\infty \cdot \mathbf{r}) \mathbf{v} - \mathbf{B}_\infty \operatorname{div} \mathbf{v} \right\} + \mathbf{r}^2 \mathbf{b} = 0. \quad (14)$$

Momentum Eq. (11) is reduced to the form

$$\frac{\partial \mathbf{v}}{\partial x} = -\mathbf{r} p - S \mathbf{B}_\infty \times \operatorname{rot} \mathbf{b}. \quad (15)$$

or its x -, y - and z - component equations are

$$\left. \begin{aligned} \frac{\partial u}{\partial x} &= -\frac{\partial p}{\partial x} - S \sin \theta (\operatorname{rot} \mathbf{b})_z \\ \frac{\partial v}{\partial x} &= -\frac{\partial p}{\partial y} + S \cos \theta (\operatorname{rot} \mathbf{b})_z \\ \frac{\partial w}{\partial x} &= -\frac{\partial p}{\partial z} - S \{ \cos \theta (\operatorname{rot} \mathbf{b})_y - \sin \theta (\operatorname{rot} \mathbf{b})_x \} \end{aligned} \right\} \quad (16)$$

Integrating the first of (16), we obtain

$$p = -u - S \sin \theta \int_{-\infty}^x (\operatorname{rot} \mathbf{b})_z dx. \quad (17)$$

Operating "rot" to (15), we obtain

$$\frac{\partial}{\partial x} \operatorname{rot} \mathbf{v} = S (\mathbf{B}_\infty \cdot \mathbf{r}) \operatorname{rot} \mathbf{b}. \quad (18)$$

Next we linearize the energy Eq. (12). $(\operatorname{rot} \mathbf{B}_*)^2 = (\operatorname{rot} \mathbf{b})^2$ is a second order small quantity, and neglecting this, (12) reduces to the equation derived without magnetohydrodynamic effect. That is, $\gamma(\gamma-1)^{-1} \partial T / \partial x = \partial p / \partial x$. Integrating this equation and putting integral constant to zero (all disturbances vanish at $x = -\infty$), we have

$$p = \gamma(\gamma-1)^{-1} T. \quad (19)$$

Linearization of the equation of state of perfect gas (9) gives

$$p = \rho T_\infty + T \quad (20)$$

From (19) and (20) we obtain

$$p = \gamma(\gamma-1)^{-1} T, \quad \rho = (\gamma-1)^{-1} (T/T_\infty), \quad p/p_\infty = \gamma \rho. \quad (21)$$

The continuity Eq. (6) is linearized to the form

$$\operatorname{div} (\rho_* \mathbf{q}_*) = \frac{\partial \rho}{\partial x} + \operatorname{div} \mathbf{v} = 0.$$

Using (21) and the first two of (16) together with the above equation we can eliminate ρ , $(\operatorname{rot} \mathbf{b})_z$ and p , then we have

$$M^2 \frac{\partial^2}{\partial x^2} (\mathbf{B}_\infty \cdot \mathbf{v}) = (\mathbf{B}_\infty \cdot \mathbf{r}) \operatorname{div} \mathbf{v} \quad (22)$$

or

$$\cos \theta \left[\frac{\partial}{\partial x} \left(\operatorname{div} \mathbf{v} - M^2 \frac{\partial u}{\partial x} \right) \right] + \sin \theta \left[\frac{\partial}{\partial y} \operatorname{div} \mathbf{v} - M^2 \frac{\partial^2 v}{\partial x^2} \right] = 0, \quad (22')$$

where M is the free stream Mach number defined by the equation $M^2 = \bar{u}_\infty^2 / (\gamma \dot{p}_\infty \bar{\rho}_\infty^{-1}) = (\gamma p_\infty)^{-1}$.

If the magnetic field is absent, (22') gives

$$\left. \begin{aligned} (1-M^2) \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0 \\ \frac{\partial}{\partial y} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) - M^2 \frac{\partial^2 v}{\partial x^2} &= 0 \end{aligned} \right\} \quad (23)$$

The first of (23) is the ordinary continuity eq., and the second can be reduced to $\partial v / \partial x - \partial u / \partial y = 0$, which is one of the equations for the condition of irrotationality. Therefore (22) seems to be reasonable generalization of the continuity condition.

2.3 Introduction of parametric function

In the previous sections, the basic equations are reduced to

induction Eq. (14) three eqs.

momentum Eq. (15) three eqs.

and

continuity Eq. (22) one eq.

These seven equations contain the seven unknown physical quantities, b_x, b_y, b_z, u, v, w and p . Of course it is possible that only one quantity, say u , is retained and the other six are eliminated from these equations. But the resulting fundamental equation in u may be inconvenient since the boundary conditions can be hardly expressed in terms of u only, and thus it can not be used to solve practical problems. For this reason it is necessary to introduce an appropriate parametric function, for which the fundamental equation is constructed together with explicit expressions of the boundary conditions.

Introducing a scalar function φ , (18) can be integrated to the form,

$$\frac{\partial \mathbf{v}}{\partial x} = S \frac{\partial \mathbf{b}}{\partial \eta} + \text{grad} \frac{\partial \varphi}{\partial x} \quad (24)$$

where

$$\frac{\partial}{\partial \eta} \equiv \mathbf{B}_{\infty} \cdot \nabla = \cos \theta \frac{\partial}{\partial x} + \sin \theta \frac{\partial}{\partial y} \quad (25)$$

We also define

$$\frac{\partial}{\partial \bar{\eta}} \equiv \sin \theta \frac{\partial}{\partial x} - \cos \theta \frac{\partial}{\partial y} \quad (26)$$

for later discussions. From (24)

$$\text{div} \mathbf{v} = \nabla^2 \varphi \quad (27)$$

is obtained. Using (24) and (27), (22) reduces to

$$\frac{\partial}{\partial \eta} \left[\left(\nabla^2 - M^2 \frac{\partial^2}{\partial x^2} \right) \varphi - M^2 S \frac{\partial}{\partial x} (\mathbf{B}_{\infty} \cdot \mathbf{b}) \right] = 0 \quad (28)$$

(14) also reduces to

$$\left(\nabla^2 \frac{\partial}{\partial x} - R_m \frac{\partial^2}{\partial x^2} + R_m S \frac{\partial^2}{\partial \eta^2} \right) \mathbf{b} + R_m S \frac{\partial}{\partial x} \left(\frac{\partial}{\partial \eta} \nabla - \mathbf{B}_{\infty} \nabla^2 \right) \varphi = 0 \quad (29)$$

We now define a new parametric function ϕ with the equations,

$$\left. \begin{aligned} \varphi &\equiv \left(\nabla^2 \frac{\partial}{\partial x} - R_m \frac{\partial^2}{\partial x^2} + R_m S \frac{\partial^2}{\partial \eta^2} \right) \Phi \\ \mathbf{b} &\equiv -R_m \frac{\partial}{\partial x} \left(\frac{\partial}{\partial \eta} \nabla - \mathbf{B}_\infty \nabla^2 \right) \Phi \end{aligned} \right\} \quad (30)$$

then (29) and $\text{div } \mathbf{b} = 0$ are satisfied automatically. Substituting (30) into (28), we obtain

$$\left[\left(R_m \frac{\partial^2}{\partial x^2} - \nabla^2 \frac{\partial}{\partial x} \right) \left(\nabla^2 - M^2 \frac{\partial^2}{\partial x^2} \right) + R_m S \left(M^2 \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial \eta^2} \right) \nabla^2 \right] \Phi = 0 \quad (31)$$

which is the fundamental equation in Φ . $\mathbf{b}$ and $\mathbf{v}$ are expressed in terms of Φ as follows;

$$\left. \begin{aligned} \mathbf{b} &= -R_m \left(\frac{\partial}{\partial \eta} \nabla - \mathbf{B}_\infty \nabla^2 \right) \frac{\partial \Phi}{\partial x} \\ \mathbf{v} &= \left[\left(\nabla^2 \frac{\partial}{\partial x} - R_m \frac{\partial^2}{\partial x^2} \right) \nabla + R_m S \mathbf{B}_\infty \nabla^2 \frac{\partial}{\partial \eta} \right] \Phi \end{aligned} \right\} \quad (32)$$

p is expressed as follows;

$$p = \left(R_m \frac{\partial^2}{\partial x^2} - \nabla^2 \frac{\partial}{\partial x} - R_m S \nabla^2 \right) \frac{\partial \Phi}{\partial x}. \quad (33)$$

Therefore all boundary conditions given with $\mathbf{b}$, $\mathbf{v}$ and p can be expressed in terms of Φ only. (31) agrees with the equation derived by Sakurai in the case of two-dimensional flow³⁾. But he neither related his parametric function (generalized stream function) to b_x and b_y nor used his fundamental equation to solve particular problems. It is rather natural because the boundary conditions are not expressed in terms of his parametric function.

2.4 Reduction of the fundamental equation (31) to some special cases

Using the above results, all the equations which have been derived by the previous writers in some particular cases can be written down easily.

2.4.1 $B_\infty = i$

(31) reduces to*

$$\left[\left(R_m \frac{\partial}{\partial x} - \nabla^2 \right) \left(\nabla^2 - M^2 \frac{\partial^2}{\partial x^2} \right) + R_m S (M^2 - 1) \nabla^2 \frac{\partial}{\partial x} \right] \Phi = 0 \quad (34)$$

(32) and (17) give

$$\left. \begin{aligned} \mathbf{b} &= R_m \left(i \nabla^2 - \frac{\partial}{\partial x} \nabla \right) \Phi \\ \mathbf{v} &= \left[\left(\nabla^2 - R_m \frac{\partial}{\partial x} \right) \nabla + i R_m S \nabla^2 \right] \Phi, \quad p = -u. \end{aligned} \right\} \quad (35)$$

Moreover if we assume $R_m \rightarrow \infty$, (34) reduces to

$$\left[\frac{(1 - M^2)(1 - N^2)}{1 - M^2 - N^2} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \Phi = 0. \quad (36)$$

(35) reduce to

* The following substitution is used without any explanatory note.

$$\Phi \text{ in (34) and (35)} = \frac{\partial}{\partial x} (\Phi \text{ in (31) and (32)}).$$

Similar unessential substitutions are often used in the following discussions without changing notation.

$$\left. \begin{aligned} b &= \left(i\mathcal{V}^2 - \frac{\partial}{\partial x} \mathcal{V} \right) \Phi \\ v &= \left(iS\mathcal{V}^2 - \frac{\partial}{\partial x} \mathcal{V} \right) \Phi, \quad p = -u, \end{aligned} \right\} \quad (37)$$

(36) is the well-known Resler's eq. On the other hand, if $R_m \rightarrow 0$ and $R_m S \equiv K = 0(1)$ we obtain from (34)

$$\left[\frac{\partial^2}{\partial x^2} + \frac{1}{1-M^2} \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + K \frac{\partial}{\partial x} \right] \Phi = 0 \quad (38)$$

(35) reduce to

$$b \sim 0, \quad v = (\mathcal{V} + iK)\Phi. \quad (39)$$

To compare (38) and (39) with the corresponding equations obtained by Sakurai in the two-dimensional case, we define a scalar function Φ' with the relation $\Phi' \equiv e^{Kx}\Phi$, then

$$\left\{ \frac{\partial^2}{\partial x^2} + K \frac{\partial}{\partial x} + \frac{1}{1-M^2} \frac{\partial^2}{\partial y^2} \right\} \Phi = e^{-Kx} \left\{ \frac{\partial^2}{\partial x^2} - K \frac{\partial}{\partial x} + \frac{1}{1-M^2} \frac{\partial^2}{\partial y^2} \right\} \Phi' = 0 \quad (40)$$

is obtained. (40), the partial differential equation in Φ' was used by Sakurai³⁾.

2.4.2 $R_m \rightarrow \infty$, $M \rightarrow 0$ and the flow is two-dimensional. (θ is arbitrary)

(31) reduces to

$$\left(\frac{\partial^2}{\partial x^2} - S \frac{\partial^2}{\partial \eta^2} \right) \mathcal{V}_2^2 \Phi = 0 \quad (41)$$

where

$$\mathcal{V}_2^2 \equiv \partial^2 / \partial x^2 + \partial^2 / \partial y^2.$$

Assuming $\Phi \equiv \Phi_1 + \Phi_2$

$$\left(\frac{\partial^2}{\partial x^2} - S \frac{\partial^2}{\partial \eta^2} \right) \Phi_1 = 0, \quad \mathcal{V}_2^2 \Phi_2 = 0 \quad (42)$$

(32) and (33) reduce to

$$\left. \begin{aligned} b &= \left(B_\infty \mathcal{V}_2^2 - \frac{\partial}{\partial \eta} \mathcal{V}_2 \right) \frac{\partial \Phi_1}{\partial x} - \mathcal{V}_2 \frac{\partial}{\partial \eta} \left(\frac{\partial \Phi_2}{\partial x} \right) \\ v &= S \left(B_\infty \mathcal{V}_2^2 - \frac{\partial}{\partial \eta} \mathcal{V}_2 \right) \frac{\partial \Phi_1}{\partial \eta} - \mathcal{V}_2 \frac{\partial}{\partial x} \left(\frac{\partial \Phi_2}{\partial x} \right) \\ p &= \left(\frac{\partial^2}{\partial x^2} - S \mathcal{V}_2^2 \right) \frac{\partial \Phi_1}{\partial x} + \frac{\partial^3 \Phi_2}{\partial x^3} \end{aligned} \right\} \quad (43)$$

Replace the dependent variable Φ_1 with F and G , and Φ_2 with ϕ as follows;

$$\left. \begin{aligned} -S \frac{\partial^3 \Phi_1}{\partial \eta \partial y \partial \eta} &\equiv \frac{\lambda_1}{1+\lambda_1^2} F(x-\lambda_1 y) + \frac{\lambda_2}{1+\lambda_2^2} G(x-\lambda_2 y) \\ -\frac{\partial^2 \Phi_2}{\partial x^2} &\equiv \phi \end{aligned} \right\} \quad (44)$$

$$\left. \begin{aligned} F &= F(x-\lambda_1 y) = F(\xi - N\eta) \\ G &= G(x-\lambda_2 y) = G(\xi + N\eta) \\ \mathcal{V}_2^2 \phi(x, y) &= 0 \end{aligned} \right\} \quad (45)$$

where the new independent variables ξ and η are defined with the relations;

when $N > 1$	when $N < 1$
wave front travelling upwards A	A'
wave front travelling downwards B	B'
$OQ = \bar{v}_{\infty} t$ $OP_1 = OP_2 = \bar{v}_m t$	$OQ' = \bar{u}_{\infty} t$ $OP'_1 = OP'_2 = \bar{v}_m t$

$$\left. \begin{aligned} F(x-\lambda_1 y) &= f_1 e^{2\pi i(x-\lambda_1 y)} \\ \phi(x, y) &= \varphi_1 e^{2\pi i(x+\lambda_1 y)} \end{aligned} \right\} \quad (50)$$

In the region $y < 0$ there is no current because the wall is insulator, and then $\mathbf{b}$ can be written in the form $\mathbf{b} = \text{grad } \phi_3$. Assume

$$b_x = \frac{\partial \phi_3}{\partial x} = 2\pi i \varphi_3 e^{2\pi i(x-\lambda_1 y)} = i \frac{\partial \phi_3}{\partial y} = i b_y. \quad (51)$$

To determine three unknown constants f_1 , φ_1 and φ_3 three conditions are necessary.

The first condition; b_y is continuous at the wall surface ($\text{div } \mathbf{b} = 0$).

$$\therefore 2\pi \varphi_3 e^{2\pi i x} = -[N/(1+\lambda_1^2)] f_1 e^{2\pi i x} - 2\pi \varphi_1 e^{2\pi i x + i\theta}. \quad (52)$$

The second condition; b_x should be continuous at the wall surface. Because a first-order surface current $\bar{\mathbf{J}}_z$ would produce first-order force component $(\bar{\mathbf{J}}_z \times \bar{\mathbf{B}}_\infty)_x$ if the magnetic field $\bar{\mathbf{B}}_\infty$ is not parallel to the x -axis. There is no mechanism here to resist such force component¹⁾.

$$2\pi i \varphi_3 e^{2\pi i x} = [-\lambda_1 N/(1+\lambda_1^2)] f_1 e^{2\pi i x} + 2\pi i \varphi_1 e^{2\pi i x + i\theta}. \quad (53)$$

The third condition; the flow velocity component normal to the wall surface is zero.

$$(1+\lambda_1^2)^{-1} f_1 e^{2\pi i x} - 2\pi \varphi_1 e^{2\pi i x} = i k \varepsilon e^{2\pi i x}. \quad (54)$$

From (52), (53) and (54) we obtain

$$\left. \begin{aligned} f_1 &= -2(1+\lambda_1^2) k \varepsilon e^{i\theta} (Ni + 2ie^{i\theta} - \lambda_1 N)^{-1} \\ \varphi_1 &= [k \varepsilon N/(2\pi)] (1+i\lambda_1) (Ni + 2ie^{i\theta} - \lambda_1 N)^{-1} \\ \varphi_3 &= [k \varepsilon N/(2\pi)] (1-i\lambda_1) e^{i\theta} (Ni + 2ie^{i\theta} - \lambda_1 N)^{-1} \end{aligned} \right\} \quad (55)$$

Using (47c), (50) and (55) the pressure on the wall surface is obtained as follows;

$$\begin{aligned} p &= -k \varepsilon e^{2\pi i x} \frac{N(i-\lambda_1) - 2\left(\frac{\lambda_1}{1+\lambda_1^2} - \frac{\sin \theta}{N}\right)(1+\lambda_1^2) e^{i\theta}}{N(i-\lambda_1) + 2ie^{i\theta}} \\ &= -k \varepsilon e^{2\pi i x} \frac{[N^3 + (N^2 - 2) \cos \theta - 2N \cos^2 \theta] - i \sin \theta [N^2 + 2N \cos \theta + 2]}{N^3 + N^2 \cos \theta + 2N \sin^2 \theta - iN(N + 2 \cos \theta) \sin \theta} \end{aligned} \quad (56)$$

$$= \left\{ \begin{array}{ll} -k \varepsilon e^{2\pi i x} & N \rightarrow \infty \\ -k \varepsilon e^{2\pi i x} (1 - 2N^{-2}) & \theta \rightarrow 0 \\ -k \varepsilon e^{2\pi i x} (N^2 - 2iN - 2)/N(N - 2i) & \theta \rightarrow \pi/2 \end{array} \right\} \quad (57)$$

The limiting values at $\theta = 0$ and $\theta = \pi/2$ agree with the results calculated by Sears and Resler¹⁾. But in the case $\theta = 0$ this agreement may be nonsense. The value of pressure disturbance shown in the second of (57) is the purely gas-dynamic one in the present theory, while in the Sears and Resler's result it must be the sum of purely gas-dynamic one and magnetic force acting on the surface current. Sears and Resler pointed out that for this case there is no interaction between the gas flow and the magnetic field except for the boundary conditions on the wall surface. The surface current, here, can be exist because the force $\bar{\mathbf{J}}_z \times \bar{\mathbf{B}}_\infty$ is normal to the wall surface.

Indeed $\theta = 0$ implies $\partial/\partial \eta = \partial/\partial x$ and so (41) reduces to $r_x^2 \Phi_{xx} = 0$ except for the particular case $S=1$. It is easy to show that (32), (33) and the other eqs. also give the following relations,

$$\begin{aligned} \mathbf{b} &= -r \Phi_{xx} = \mathbf{v}, & p &= -u, \\ \text{rot } \mathbf{b} &= 0 = \mathbf{j}, & \text{rot } \mathbf{v} &= 0 \end{aligned}$$

which are nothing else than the Sears and Resler's assertion. $\theta=0$ is say, a "singular point" in the solution (47).

§ 4. Concluding Remarks

General theory of electrically conducting perfect gas past a thin body is presented under the assumptions that the flow is inviscid, steady and three-dimensional, and that the magnetic Reynolds number and the direction of applied field are arbitrary. The magnetic field, the flow velocity and the pressure are all connected to the "parametric function" for which the "fundamental equation" is derived. Therefore the boundary conditions are also can be expressed in terms of the parametric function. This fundamental equation is reduced easily to those obtained by previous writers in respective particular cases. The general theory is applied to the wavy wall problem in the case where the magnetic field is applied in an arbitrary direction. It is found that the disturbance wave may travel forward when Alfvén number is less than unity.

The author would like to acknowledge his gratitude for the cordial guidances and discussions on the work described in this paper given by Prof. Tani, Prof. Tamada and Mr. Sakurai.

Appendix. The Slender-Body Approximation

For the slender-body approximation both L_y/L_x and L_z/L_x are very small, where L_x , L_y and L_z are the characteristic lengths in the x -, y - and z - directions respectively. Assume that the operator $\partial/\partial x$ is a ordinary quantity ($=O(\varepsilon^0)$) and that $\partial/\partial y$ and $\partial/\partial z$ are the same order large quantities ($=O(\varepsilon^{-1})$), then generally $\partial^{m+n+\nu}/\partial y^m \partial z^n \partial x^\nu$ is the $(m+n)$ th order large quantity ($=O(\varepsilon^{-(m+n)})$). Thus, retaining only the highest order large quantities in Eqs. (31), (32) and (33), we have the following expressions as the slender-body approximation in magneto-dynamics

$$\left[\left(\frac{\partial}{\partial x} + R_m S \sin^2 \theta \right) \frac{\partial^2}{\partial y^2} + \frac{\partial}{\partial x} \frac{\partial^2}{\partial z^2} \right] \mathcal{F}_2^2 \Phi = 0 \quad (O(\varepsilon^{-4}) \text{ in (31)}) \quad (A1)$$

$$\left. \begin{aligned} b_x &= R_m \cos \theta \mathcal{F}_2^2 (\partial \Phi / \partial x) \\ b_y &= R_m \sin \theta \partial^3 \Phi / \partial x \partial z^2 \\ b_z &= -R_m \sin \theta \partial^3 \Phi / \partial x \partial y \partial z \end{aligned} \right\} \quad (O(\varepsilon^{-2}) \text{ in (32)}) \quad (A2)$$

$$\left. \begin{aligned} u &= (R_m S / 2) \sin 2\theta \mathcal{F}_2^2 (\partial \Phi / \partial y) \\ v &= \mathcal{F}_2^2 \left(\frac{\partial}{\partial x} + R_m S \sin^2 \theta \right) (\partial \Phi / \partial y) \\ w &= \mathcal{F}_2^2 (\partial^2 \Phi / \partial x \partial z) \end{aligned} \right\} \quad (O(\varepsilon^{-3}) \text{ in (33)}) \quad (A3)$$

where

$$\mathcal{F}_2^2 \equiv \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (A4)$$

Note that $\mathcal{F}_2^2$ defined here is different from $\mathcal{F}_2^2$ used in section 2.4.2. It is found easily from (A2) and (A3) that the relations

$$\frac{\partial b_y}{\partial y} + \frac{\partial b_z}{\partial z} = 0, \quad \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad (A5)$$

are valid.

When the magnetic effect is absent (that is, $R_m=0$ and $S=0$), we have $\mathcal{F}_2^2(\mathcal{F}_2^2 \Phi_x)=0$, $\mathbf{b}=0$, $u=0$, $v=(\partial/\partial y)(\mathcal{F}_2^2 \Phi_x)$ and $w=(\partial/\partial z)(\mathcal{F}_2^2 \Phi_x)$ from (A1), (A2) and (A3). Putting $\Phi' \equiv \mathcal{F}_2^2 \Phi_x$, these relations represent the ones for the conventional slender-body approximation.

References

- 1) W. R. Sears and E. L. Resler Jr.: *Theory of Thin Airfoils in Fluids of High Electrical Conductivity*; J. Fluid Mech. **5**, 2 (1959/2) 257-273.
- 2) W. R. Sears: *Magnetohydrodynamic Effects in Aerodynamic Flows*; (General Lecture, Proceedings of the Eighth Japan National Congress for Applied Mechanics 1958) 1-39.
- 3) T. Sakurai: *Two-dimensional Flow of Ideal Gas with Electric Conductivity past a Thin Wing*; Preprint for the Fourth Meeting on Applied Mathematics and Mechanics in Japan 1959 May. (In Japanese)

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 1, JANUARY, 1960

Condenser Microphones with Plastic Diaphragms for Airborne Ultrasonics, II

By Kiichiro MATSUZAWA

*Department of Physics, Faculty of Science and Literature,
Ehime University*

(Received August 18, 1959)

A detailed study is made on the condenser microphones with back plates named 'group IA' in Part I of the present paper.

For each back plate, the surface roughness is studied by using profilograms and the distribution function of the surface profile is obtained. Formulae for the resonance frequency, the electrostatic capacitance and the low frequency sensitivity are obtained theoretically assuming a simple model microphone with a back plate having a profile represented by the above distribution function. The formulae are found to be in fairly good agreement with the experiments.

§ 1. Introduction and Conclusion

As reported in Part I (cited as (I) in the following) of this paper¹⁾, various condenser microphones with plastic diaphragms for airborne ultrasonics have been classified into two groups based on the surface roughness of the back plates, i.e. 'group I' and 'group II', and they have been further classified into some sub-groups.

In the present paper, a detailed study is made on the condenser microphones of group IA (the microphones IA-1~IA-4 in (I)) with back plates having finely, uniformly roughened surfaces.

For each back plate, the surface roughness is studied by using profilograms and the distribution function of the surface profile is obtained. Formulae for the resonance frequency, the electrostatic capacitance and the low frequency sensitivity are obtained theoretically by use of a simple model microphone

with a back plate having a profile represented by the function, assuming that the plastic diaphragm acts dynamically as a mass and the layer of air between the diaphragm and the back plate acts dynamically as a cushion. It is found that the formulae are in fairly good agreement with the experiments except the microphones IA-4.

The directional characteristics of the microphones of group IA are found to be almost independent of whether the value of the push-out of the back plates δ is 0.55mm or 0.4mm. The directional characteristics are also shown to be explained approximately by the theory using another simple model microphone, whose construction is assumed to be uniform all over the surface of the back plate.

§ 2. Surface Profiles of Back Plates

Profilograms of each back plate were taken along three diameters making an angle of 60°

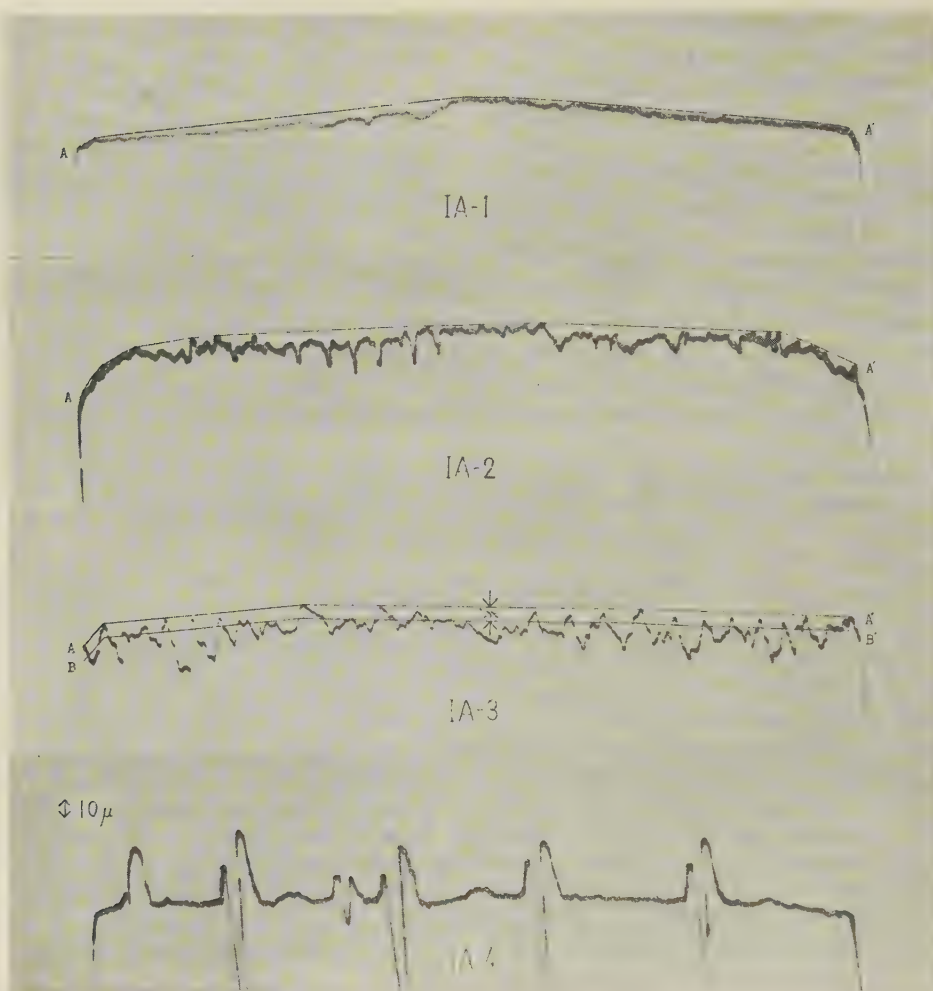


Fig. 1. Profilograms of back plates. Bent lines AA' show cross-sections of imaginary planes contacting with surfaces of back plates.

with each other, and they were found to be similar to each other. Some examples are shown in Fig. 1. In these profilograms the vertical magnification is about 28 times larger than the horizontal one. As seen in Fig. 1, the surface roughnesses of the back plates IA-1~IA-3 are similar to each other, but that of the back plate IA-4 is somewhat different from those of IA-1~IA-3. Therefore, the back plate IA-4 will be treated separately in the following.

For the back plates IA-1~IA-3, we assume two-dimensional back plates having cross-sections represented by the profilograms as shown in Fig. 1 respectively. The bent lines AA' drawn on the profilograms show the cross-sections of imaginary planes contacting with the surfaces of the back plates. The

bent line BB' as shown in Fig. 1, IA-3, for instance, is drawn parallel to AA', $y'(\mu)$ being the distance between AA' and BB'. Thus, by using the profilogram, the relation between y' and x is studied statistically, where x is the ratio of the surface area, projected on AA', of the back plate above BB' to the total projected area. The relations between x and y ($=C_0-y'$) are shown in Fig. 2, where C_0 is a constant to be determined such that $x=1/2$ at $y=0$. It is known in general that for mechanically-treated surfaces there exists a relation between x and y of the form²⁾:

$$x = \frac{1}{2} - \frac{1}{\sqrt{\pi}} \int_0^{y/h} \exp(-t^2) dt, \quad (2.1)$$

where h is $\sqrt{2}$ times of the standard devi-

ation of Gaussian distribution of a surface profile. The solid lines in Fig. 2 were obtained by (2.1), using the values of h tabulated in the second column of Table I. Thus, the surface roughnesses of the back plates IA-1 ~IA-3 may be represented by (2.1) statistically.

Next, the surface roughness of the back

plate IA-4 was studied as follows. For the sake of simplicity, each small dip with ring margine on the surface of the back plate, whose cross-section is shown by solid lines in Fig. 3, is replaced by a circular cone having a coaxial, cylindrical hollow as shown by broken lines. Then, the relation between the vertical distance $y(\mu)$ from a point P on the conical surface to the flat plane of the back plate, and the ratio x of the surface area,

Table I. Constants of back plates.

Back plate	h (μ)	d_s (μ)	a	b (μ)
IA-1	2.5	3.9	0.015	3.8
IA-2	6.5	8.1	0.049	7.6
IA-3	8.5	10.0	0.063	9.2
IA-4	—	20.2	0.067	21.7

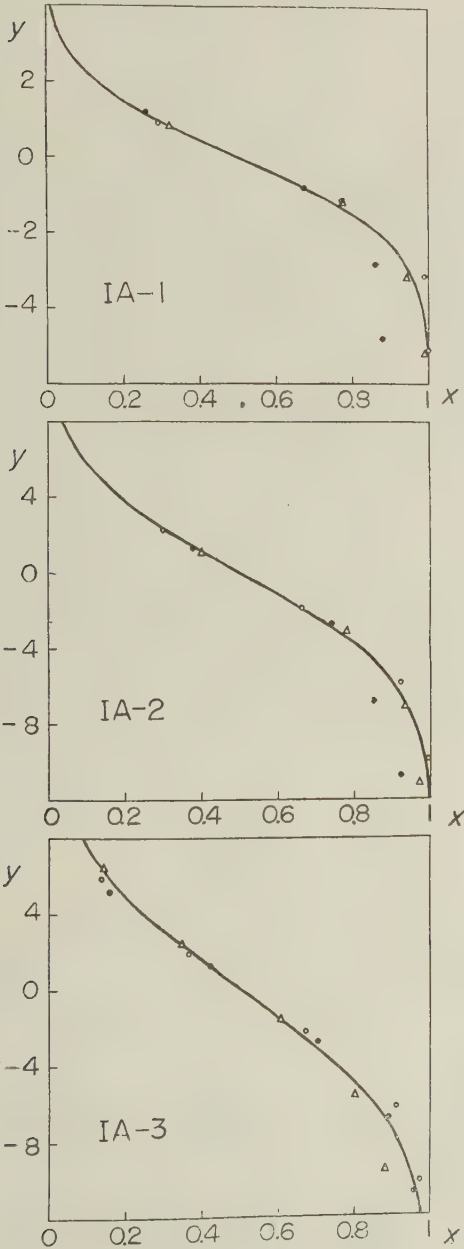


Fig. 2. Statistical distributions of surface roughnesses of back plates.
●, ○, △ measurements for different sections.
— calculated by (2.1).

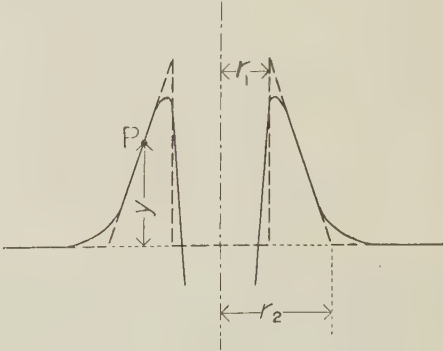


Fig. 3. Cross-section of the surface of the back plate IA-4.

projected on the flat plane, of the back plate above the point P to the total projected area, is given by

$$x = N\pi \left\{ \left(r_2 - \frac{y}{m} \right)^2 - r_1^2 \right\},$$
$$0 \leq y \leq m(r_2 - r_1), \quad (2.2)$$

where r_1 is the radius of the cylindrical hollow, r_2 the radius at the bottom of the cone, m the slope of the generating line of the cone, and N the number of dips with ring margines per unit area of the surface. The values of these quantities were determined by measurements as: $r_1=0.013$ cm, $r_2=0.030$ cm, $m=2200 \mu/\text{cm}$ and $N=91$. It is to be noted that the small dips are conical hollows of about 130μ in depth.

§ 3. Theoretical Discussions

i) Resonance frequency, electrostatic capacitance and low frequency sensitivity

In order to study the microphones with the back plates IA-1~IA-3 theoretically, a simple model microphone having a two-dimensional back plate has been proposed, whose profile is represented by the distribution function (2.1). The cross-section of this model microphone is shown in Fig. 4. $P(x, y)$ is a point

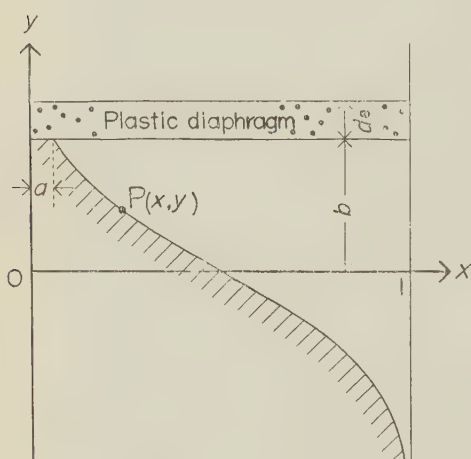


Fig. 4. Cross-section of the model microphone.

on the curve represented by (2.1). It is assumed that the back plate touches the diaphragm at the point (a, b) . For convenience' sake, the effective thickness $d_e(\mu)$ of the diaphragm was adopted instead of the mechanical thickness. Further, it was assumed that the diaphragm acts dynamically as a mass and the air between the diaphragm and the back plate acts dynamically as a cushion.

The mean thickness $d_a(\mu)$ of the layer of air for $a \leq x \leq 1$ is given by

$$d_a(1-a) = \int_a^1 (b-y) dx. \quad (3.1)$$

Using (2.1) and (3.1) we obtain

$$\frac{d_a}{h} = \frac{b}{h} + \frac{\exp(-b^2/h^2)}{\sqrt{\pi} + 2 \int_0^{b/h} \exp(-t^2) dt}. \quad (3.2a)$$

The stiffness of the air cushion per unit area of the model back plate is represented by $K(1-a)/d_a$, where $K (=1.01 \times 10^6 \text{ dyne/cm}^2)$ is the bulk modulus of air, and $M (\text{mg/cm}^2)$ is the surface density of the diaphragm.

Then, the resonance frequency f (kc/s) of the microphone is given by

$$f = \frac{1}{2\pi} \sqrt{\frac{10K}{d_a M}} = \frac{506}{\sqrt{d_a M}}. \quad (3.3)$$

The electrostatic capacitance of the microphone per unit area of the back plate $C (\mu\text{F/cm}^2)$ is given by

$$C = 885 \left(\frac{a}{d_e} + \int_a^1 \frac{dx}{d_e + b - y} \right). \quad (3.4a)$$

Under a sound pressure p (μbar), a uniform displacement Δb ($|\Delta b| \ll d_e + b - y$) of the diaphragm occurs except the parts in contact with the back plate. Accordingly, the electrostatic capacitance C varies by ΔC , and the voltage between the two electrodes of the microphone, being E ($=200 \text{ V}$) for $p=0$, varies by ΔE . Then, making use of the well-known relations $p = -K\Delta b/d_a$, $\Delta E/E = -\Delta C/C$ and $S = 20 \log_{10} |\Delta E/p|$, we obtain the expression for the low frequency sensitivity S (dB rel. 1V/ μbar) of the microphone as:

$$S = -74.1 + 20 \log_{10} \left\{ d_a \frac{885}{C} \int_a^1 \frac{dx}{(d_e + b - y)^2} \right\}. \quad (3.5a)$$

For the microphones IA-4, the distribution function (2.2) is used and discussions similar to those for the microphones IA-1~IA-3 are carried out. Namely, substituting (2.2) into (3.1), (3.4a) and (3.5a), we obtain the following relations respectively:

$$(d_a - b) \left[1 - N\pi \left\{ \left(r_2 - \frac{b}{m} \right)^2 - r_1^2 \right\} \right] + \frac{2N\pi}{m} \left(\frac{r_2 b^2}{2} - \frac{b^3}{3m} \right) = 0, \quad (3.2b)$$

$$C = 885 \left[\frac{a}{d_e} + \frac{1 - N\pi(r_2^2 - r_1^2)}{d_e + b} + \frac{2N\pi}{m^2} \left\{ b + (mr_2 - b - d_e) \ln \frac{d_e + b}{d_e} \right\} \right], \quad (3.4b)$$

and

$$S = -74.1 + 20 \log_{10} \left[d_a \frac{885}{C} \left\{ \frac{1 - N\pi(r_2^2 - r_1^2)}{(d_e + b)^2} + \frac{2N\pi}{m^2} \left(\frac{mr_2 - b - d_e}{b + d_e} \cdot \frac{b}{d_e} + \ln \frac{d_e + b}{d_e} \right) \right\} \right]. \quad (3.5b)$$

ii) Directional characteristics

We have assumed another simple model

microphone, whose construction is uniform all over the surface of the back plate, such that if the effective area of the diaphragm is divided into many local regions, each of the local regions corresponds to a local condenser microphone and the pressure response of the local microphones is equal to each other.

As is well known, the theoretical directional characteristics of such a model microphone in an infinite baffle, being equal to those of a sound source acting as a piston in an infinite baffle, are given by

$$\left. \begin{aligned} R &= |2J_1(x)/x|, \\ x &= 2\pi r/\lambda \cdot \sin \gamma, \end{aligned} \right\} \quad (3.6)$$

where $J_1(x)$ is the Bessel function, r the effective radius of the diaphragm, λ the wavelength of the sound, and R the magnitude of the ratio of the sensitivity for obliquely incident sound at an angle of γ to that for normal incidence, i.e. at $\gamma=0$.

For high frequencies, as is generally known, the directional characteristics within some values of γ are almost independent of whether the baffle is used or not. To check these ranges, the directional characteristics of our microphones with and without baffle were measured. Some results are shown in Fig. 5. It will be seen that above ca. 40 kc/s the effects of the baffle are almost inappreciable in the ranges of γ necessary for the discussion in § 4, ii). Accordingly, the theoretical directional characteristics of our model microphone may be given by (3.6) for high frequencies above ca. 40 kc/s.

For low frequencies, however, instead of the theoretical directional characteristics, the experimental ones of an MR-103 condenser microphone with the capsule mentioned in (I) were used, because the diaphragm of the MR-103 microphone can be considered to act as a piston approximately and the shape of the MR-103 microphone with the capsule is similar to our microphones.

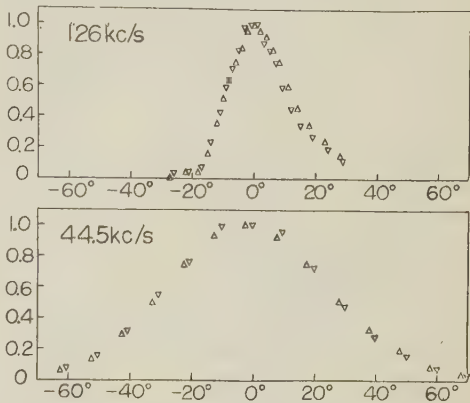


Fig. 5. Effect of baffle upon directional characteristics. Magnitude of the relative sensitivity versus angle of incidence.
△ without baffle.
▽ in a baffle (13×13 cm²).

§ 4. Experimental Results and Discussions

- i) Resonance frequency, electrostatic capacitance and low frequency sensitivity
- In addition to the eleven microphones with the back plates of group IA as shown in

Table II. Details of microphones with back plates of group IA.

Back plate	Construction of microphone			Capacitance of microphone ($\mu\mu\text{F}$)	Frequency response of microphone			Symbol of microphone
	Material	Surface density	Effective thickness		Q-factor	Resonance frequency f (kc/s)	Low frequency sensitivity S (dB rel. 1V / μbar)	
		M (mg/cm ²)	d_e (μ)					
IA-1	25 μ Polyester	5.0	7.3	88.5	3.1	113	-86.5	(A)
	25 μ Polyester	3.8	6.7	78	3.3	130	-84.0	
IA-2	13 μ Polyester	3.0	4.1	92	2.0	103	-81.5	(B)
IA-3	13 μ Polyester	2.3	3.7	74	2.5	101	-78.5	(C)
	6 μ Polyester	1.8	2.2	97.5	2.5	125	-75.5	
IA-4	13 μ Polyester	1.8	3.9	49.5	2.1	81	-81.0	(D)

Table III in (I), six microphones as shown in Table II were also examined. The first~eighth columns of Table II correspond to the same columns of Table III in (I) respectively. In the ninth column, there is shown the symbol of the microphone, to which we shall refer in § 4, ii).

The values of d_a were calculated by using (3.3) and the experimental values of M and f as shown in Table III in (I) and in Table II.

The results are given in the third column of Table I.

For the microphones IA-1~IA-3, the values of a and b were obtained from (3.2a) by using the values of h and d_a in Table I. For the microphones IA-4, the values of a and b were obtained from (3.2b) by using (2.2) and the value of d_a in Table I. Although Eq. (3.2b) has three real roots with respect to b , only one root is adopted which satisfies the relation $0 < b < m(r_2 - r_1)$. The values of a and b thus obtained are shown in the fourth and fifth columns of Table I respectively.

The values of the low frequency sensitivity S and the effective thickness d_e as tabulated in Table III in (I) and in Table II are shown graphically in Fig. 6. The values of C calculated from the electrostatic capacitance shown in these tables are also plotted against d_e in Fig. 6. For the microphones IA-1~IA-3, the theoretical curves for S and C as shown in Fig. 6 were obtained by using (3.5a) and (3.4a) respectively after some tedious calculations involving numerical integrations, where the relation (2.1) and the values of a , b , d_a and h as tabulated in Table I were used. For the microphones IA-4, the theoretical curves for S and C in Fig. 6 are obtained in the same way by (3.5b) and (3.4b) respectively.

Allowing for some errors, it is seen that the coincidence of our theory using the simple model microphone mentioned in § 3, i) with the experiments is fairly good for the microphones IA-1~IA-3. Therefore, it may be concluded that the relation $f \propto M^{-1/2}$ and the relation between S and d_e hold good also for the microphones IA-1 as mentioned in (I). This conclusion is also ascertained by the additional experiments in Table II.

Thus, if we can determine the constant a or b for a back plate having a surface profile represented by the Gaussian distribution statistically, then we can predict by the present theory the resonance frequency f , the electrostatic capacitance C and the low frequency sensitivity S of a microphone composed of the back plate and any diaphragm of given physical properties such as surface density M and effective thickness d_e .

For the microphones IA-4, there is a disagreement between the theory and the experiments, so further investigations on the

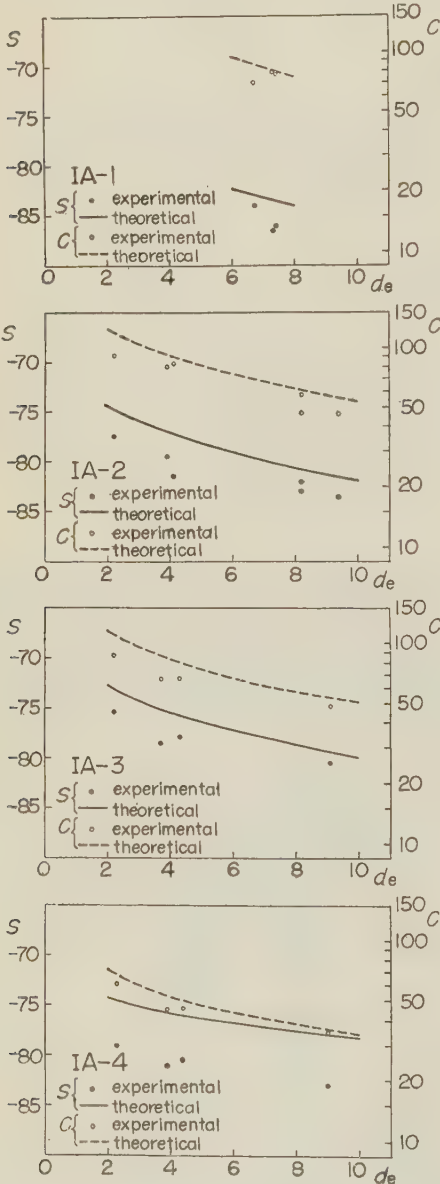


Fig. 6. Low frequency sensitivity S in dB rel. $1V/\mu\text{bar}$ and electrostatic capacitance of microphone per unit area of back plate C in $\mu\mu\text{F}/\text{cm}^2$ versus effective thickness d_e in μ of diaphragm.

model are required.

ii) Directional characteristics

The directional characteristics of the four microphones (A), (B), (C) and (D) as shown in Table II were measured as the representatives of group IA.

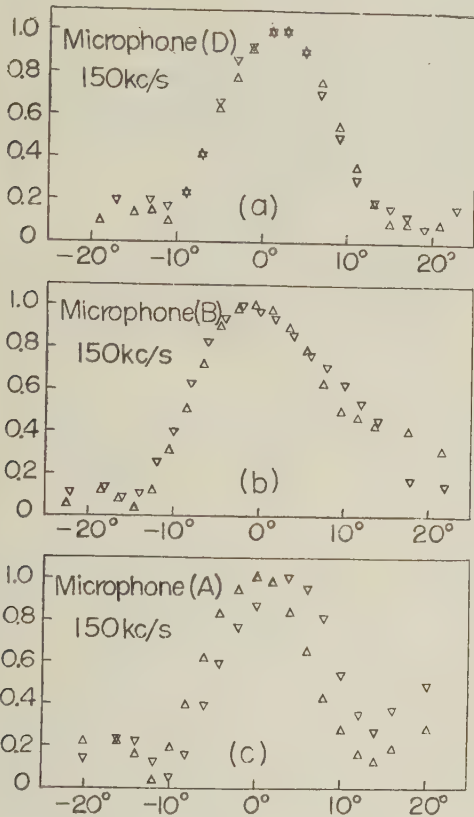


Fig. 7. Effect of δ upon directional characteristics. Magnitude of the relative sensitivity versus angle of incidence.
 $\triangle \delta = 0.4$ mm.
 $\nabla \delta = 0.55$ mm.

To examine the dependence of the directional characteristics upon the push-out of the back plates δ , the directional characteristics of these four microphones at $\delta = 0.55$ mm and $\delta = 0.4$ mm were measured at seven frequencies ranging from 22 to 150 kc/s. Some results are shown in Fig. 7. In the eighteen cases, for example, as shown in Fig. 7(a) the directional characteristics are independent of δ , and in the eight cases as shown in Fig. 7(b) they are almost independent of δ , but in the two cases they depend considerably on δ as shown in Fig. 7(c). On the whole, the effects

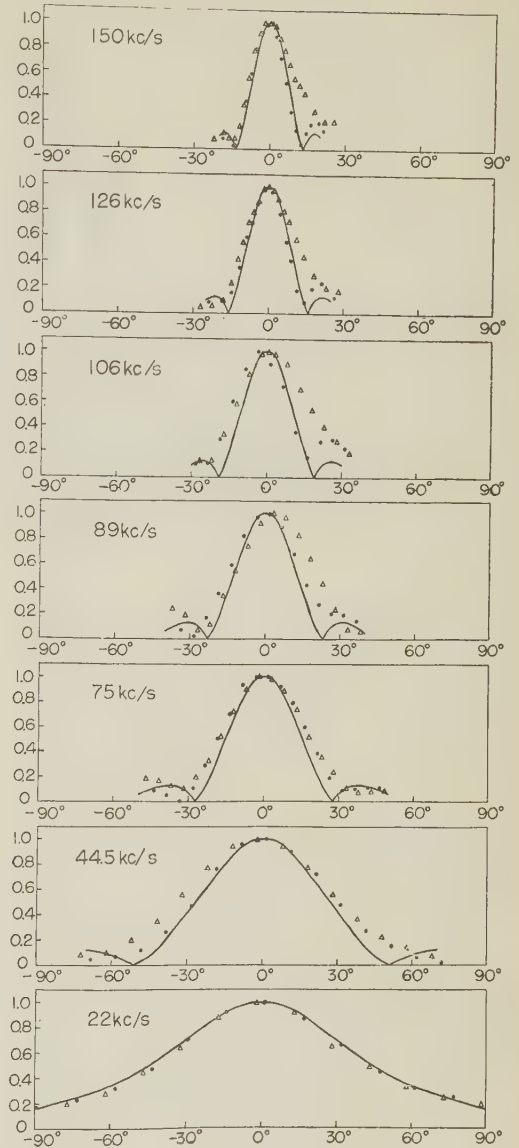


Fig. 8. Directional characteristics of the microphone. Magnitude of the relative sensitivity versus angle of incidence.
 $\bullet$ microphone (C).
 $\triangle$ microphone (B).
— theory.

of δ upon the directional characteristics are very small. Accordingly, only the mean of the two directional characteristics at $\delta = 0.55$ mm and $\delta = 0.4$ mm may be used in the following discussions.

The mean directional characteristics of the microphones (C) and (B) thus obtained are shown in Fig. 8. The solid lines in Fig. 8

are the theoretical directional characteristics mentioned in § 3, ii). The directional characteristics of the microphone (C) are in the best agreement with the theory among the four microphones, while those of the microphone (B) are in the poorest agreement with it.

Allowing for some errors, the experiments for the microphone (C) are in fairly good agreement with the theory excepting the case of the frequency 106 kc/s. The experiments for the microphone (B) agree with the theory approximately below 75 kc/s, but they show some deviations from the theory above 89kc/s. On the whole, however, the directional characteristics of our microphones might be explained approximately by the theory using the simple model microphone mentioned in § 3, ii).

Acknowledgements

The writer wishes to express his cordial thanks to Professor S. Tomotika for his continual guidance and also for his kind inspection of the manuscript. The writer's thanks are also due to Dr. O. Nomoto of the Kobayasi Institute of Physical Research for useful advice and discussions. Also, the writer is indebted to Mr. Yoshihide Oonishi of the Faculty of Technology of Ehime University for his help in taking the profilograms and for his invaluable discussions on the mechanical surface roughness.

References

- 1) K. Matsuzawa: J. Phys. Soc. Japan **13** (1958) 1533.
- 2) Y. Kattō: Trans. Japan Soc. Mech. Engrs. **22** (1956) 693 (in Japanese).

A Linearized Theory of Magnetohydrodynamic Flow past a Fixed Body in a Parallel Magnetic Field

By HIROWO YOSINOBU

*Junior College of Engineering, University of Osaka Prefecture,
Neyagawa, Osaka*

(Received August 27, 1959)

In the present paper is studied the flow of a viscous, incompressible and electrically conducting fluid past a fixed body in the presence of a parallel magnetic field. A perturbation method similar to Oseen approximation in ordinary hydrodynamics is applied to both the flow field and the magnetic field. It proves that the pressure number (namely, the ratio of the magnetic pressure to the dynamic pressure) plays an important role to determine the main features of the field. Detailed calculations are carried out for the flow past a circular cylinder and an approximate formula for the drag per unit span of the cylinder is obtained.

§1. Introduction

The flow of a viscous, incompressible and electrically conducting fluid past a fixed body in the presence of a parallel magnetic field was first studied by Chester¹⁾. He treated the flow past a sphere in a limiting case where both the Reynolds number and the magnetic Reynolds number were vanishingly small, while the pressure number was infinitely large so that the Hartmann number was finite. Analysis was carried out by applying Stokes approximation to both the modified Navier-Stokes equation and the induction equation, and the drag was given in a power series of the Hartmann number. It can be seen in his results that the presence of the magnetic field increases the drag.

Kakutani and the present writer²⁾ applied his ideas to the two-dimensional flows past a circular cylinder in the parallel and the transverse magnetic fields. Appropriate solutions were obtained for both cases, while in ordinary hydrodynamics Stokes approximation gives no acceptable solution for the two-dimensional flow.

In the present paper is studied the flow past a fixed body in a parallel magnetic field at finite Reynolds and magnetic Reynolds numbers with finite pressure number. In order to solve the modified Navier-Stokes equation and the magnetic equation, an approximate method of solution similar to Oseen approximation in ordinary hydrodynamics is proposed. The equations are first linearized by a perturbation method and then solved under appropriate

conditions.

It proves from the asymptotic behaviours of the field that there may be three distinct types of the field according as the pressure number (namely, the ratio of the characteristic magnetic pressure to the characteristic dynamic pressure) is greater than, equal to or smaller than unity.

Detailed calculations are carried out only for the flow past a circular cylinder. Drag experienced by the unit span of the cylinder is calculated to the first order of small Reynolds and magnetic Reynolds numbers. The numerical values for various values of the pressure number are computed for several values of the Reynolds and the magnetic Reynolds numbers. Similar calculations are also carried out for the flow past a sphere by Gotoh³⁾ and are published in a subsequent paper.

§2. Fundamental Equations and their Linearization

In a great number of magnetohydrodynamic problems the hydrodynamic equations and the electromagnetic equations must be solved simultaneously, since the interaction between the motion of the fluid and the magnetic field must be taken into account. When an electrically conducting fluid passes across a line of magnetic induction, electric current is induced, which causes a rotational magnetic field. On the other hand, the current, coupled with the magnetic field, yields a body force acting on the fluid, the so-called Lorentz force, which controls the motion of the fluid.

Now, we shall consider the motion of a viscous, incompressible and electrically conducting fluid. The governing equations for the motion of the fluid are the modified Navier-Stokes equation:

$$\rho \frac{\partial \mathbf{V}}{\partial t} + \rho(\mathbf{V} \cdot \text{grad}) \mathbf{V} = -\text{grad } P + \rho \nu \Delta \mathbf{V} + q \mathbf{E} + \mathbf{J} \times \mathbf{B}, \quad (2.1)$$

and the equation of continuity:

$$\text{div } \mathbf{V} = 0. \quad (2.2)$$

And those for the electromagnetic field are the Maxwell equations:

$$\text{curl } \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}, \quad (2.3) \quad \text{div } \mathbf{B} = 0, \quad (2.4)$$

$$\text{curl } \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (2.5) \quad \text{div } \mathbf{D} = q, \quad (2.6)$$

with Ohm's law:

$$\mathbf{J} = \sigma(\mathbf{E} + \mathbf{V} \times \mathbf{B}) + q \mathbf{V}, \quad (2.7)$$

where the quantities of the field and the physical constants of the fluid have been written in the usual notations and should be measured by the rationalized M.K.S. units.

We assume the fluid to be electromagnetically homogeneous and isotropic, so that the magnetic induction $\mathbf{B}$ and the electric displacement $\mathbf{D}$ are connected with the magnetic field $\mathbf{H}$ and the electric field $\mathbf{E}$ by the following relations respectively:

$$\mathbf{B} = \mu \mathbf{H}, \quad (2.8)$$

$$\text{and } \mathbf{D} = \varepsilon \mathbf{E}, \quad (2.9)$$

where μ and ε are the magnetic permeability and the dielectric constant of the fluid respectively, and are both constant throughout the fluid. The electric conductivity σ is also supposed to be constant throughout the fluid.

In usual magnetohydrodynamic problems, the term of the displacement current $\partial \mathbf{D} / \partial t$ in (2.3) and the terms involving the excess charge q in (2.1) and (2.7) can be neglected, as shown by Batchelor⁽¹⁾, unless relativistic effects are appreciable. Then, substituting (2.7) into (2.3), we have

$$\text{curl } \mathbf{H} = \sigma(\mathbf{E} + \mathbf{V} \times \mathbf{H}). \quad (2.10)$$

Hereafter, we shall confine ourselves to the problem of the steady flow past a fixed body in the parallel magnetic field, so that all derivatives of the field quantities with respect to time disappear. The magnetic field and the velocity of the fluid being uniform and parallel to each other at infinity, the electric field $\mathbf{E}$ in (2.10) must vanish there. Then, one of the

possible solutions for Eq. (2.5) is

$$\mathbf{E} = 0, \quad (2.11)$$

which yields in (2.6)

$$q = 0. \quad (2.12)$$

It was shown in our previous paper that (2.11) and (2.12) are unique solution for the two-dimensional flow. The same is true for the axially symmetric flow, as will be shown in the subsequent paper⁽³⁾. If we assume $q = 0$ in the whole field, (2.11) is an appropriate solution for the present problem.

Then, (2.10) is reduced to

$$\text{curl } \mathbf{H} = \sigma \mu \mathbf{V} \times \mathbf{H}. \quad (2.13)$$

Bearing (2.3) in mind and substituting (2.13) into (2.1), we have

$$\rho(\mathbf{V} \cdot \text{grad}) \mathbf{V} = -\text{grad } P + \rho \nu \Delta \mathbf{V} + \sigma \mu^2 (\mathbf{V} \times \mathbf{H}) \times \mathbf{H}. \quad (2.14)$$

Thus, we have obtained the fundamental equations (2.13) and (2.14) for the present problem in terms of $\mathbf{H}$, $\mathbf{V}$ and P , which should be solved simultaneously in combination with the equations (2.2) and (2.4).

We shall next consider the boundary conditions to be satisfied by $\mathbf{H}$ and $\mathbf{V}$. Since the magnetic field and the velocity of the fluid are supposed to be uniform and parallel to each other at infinity, the boundary conditions at infinity are

$$\mathbf{H} = H_0 \mathbf{i} \quad \text{and} \quad \mathbf{V} = V_0 \mathbf{i}, \quad (2.15)$$

where $\mathbf{i}$ is the unit vector in the direction of the undisturbed magnetic field or the undisturbed velocity, the constants H_0 and V_0 being their magnitudes respectively. The condition to be satisfied by $\mathbf{V}$ at the surface of the fixed body is the same as in ordinary hydrodynamic problems, namely:

$$\mathbf{V} = 0. \quad (2.16)$$

On the other hand, the magnetic field must be continued into the body through the following conditions at the surface of the body,

$$\left. \begin{aligned} \mu \mathbf{H}_+ &= \mu^* \mathbf{H}_+^*, \\ \mathbf{H}_\parallel &= \mathbf{H}_\parallel^*, \end{aligned} \right\} \quad (2.17)$$

where $\mathbf{H}^*$ is the magnetic field inside the body, μ^* the magnetic permeability of the body, and the subscripts $\perp$ and $\parallel$ denote 'the normal and the tangential components of' the magnetic field at the surface of the body respectively.

Thus, it becomes necessary to give the magnetic field inside the body. Since the

electric field $\mathbf{E}$ and the velocity $\mathbf{V}$ in (2.10) are both zero inside the body, the magnetic field $\mathbf{H}^*$ is subject to

$$\text{curl } \mathbf{H}^* = 0, \quad (2.18)$$

which should be solved in combination with the equation:

$$\text{div } \mathbf{H}^* = 0. \quad (2.19)$$

The present problem is reduced to solving the simultaneous equations (2.2), (2.4), (2.13) and (2.14) outside the body and the equations (2.18) and (2.19) inside the body, under the boundary conditions (2.15), (2.16) and (2.17). In general, it is difficult to solve them directly, since the equations (2.13) and (2.14) are non-linear in $\mathbf{H}$ and $\mathbf{V}$. Hence, we should devise some appropriate methods of linearization of these equations to solve them approximately. The extended Stokes approximation proposed by Chester¹⁾ is obviously one of these methods. However, it can be applied only to flows at infinitely small Reynolds and magnetic Reynolds numbers with infinite pressure number.

For flows at finite Reynolds and magnetic Reynolds numbers with finite pressure number, we should devise another method of linearization. The velocity field is uniform at infinity and is disturbed near the body, which will cause a corresponding disturbance in the magnetic field. Hence, we may propose a method of linearization similar to Oseen approximation in ordinary hydrodynamics.

We assume that the velocity and the magnetic field can be represented as

$$\left. \begin{aligned} \mathbf{V} &= V_0 \mathbf{i} + \mathbf{v}, \\ \mathbf{H} &= H_0 \mathbf{i} + \mathbf{h}, \end{aligned} \right\} \quad (2.20)$$

and respectively, where $\mathbf{v}$ and $\mathbf{h}$ are perturbed velocity and magnetic field, and are assumed to be small compared with the undisturbed velocity V_0 and the undisturbed magnetic field H_0 , respectively. Substituting (2.20) into (2.13) and (2.14), and neglecting the square terms in $\mathbf{v}$ and $\mathbf{h}$, we have the following sets of the linearized equations in non-dimensional forms:

$$\left\{ \begin{aligned} \frac{\partial h}{\partial y} - \frac{\partial g}{\partial z} &= 0, \end{aligned} \right. \quad (2.21)$$

$$\left\{ \begin{aligned} \frac{\partial f}{\partial z} - \frac{\partial h}{\partial x} &= R_m(w - h), \end{aligned} \right. \quad (2.22)$$

$$\left\{ \begin{aligned} \frac{\partial g}{\partial x} - \frac{\partial f}{\partial y} &= R_m(-v + g), \end{aligned} \right. \quad (2.23)$$

$$\left\{ \begin{aligned} R \frac{\partial u}{\partial x} &= -\frac{\partial p}{\partial x} + \nabla^2 u, \end{aligned} \right. \quad (2.24)$$

$$\left\{ \begin{aligned} R \frac{\partial v}{\partial x} &= -\frac{\partial p}{\partial y} + \nabla^2 v + M^2(g - v), \end{aligned} \right. \quad (2.25)$$

$$\left\{ \begin{aligned} R \frac{\partial w}{\partial x} &= -\frac{\partial p}{\partial z} + \nabla^2 w + M^2(h - w), \end{aligned} \right. \quad (2.26)$$

where (x, y, z) are the non-dimensional coordinate variables referring to the characteristic length of the body, L_0 say, the origin of the coordinates being chosen at a point inside the body and the x -axis in the direction of $\mathbf{i}$, (f, g, h) and (u, v, w) are the x, y, z -components of the non-dimensional perturbed magnetic field $\mathbf{h}/H_0$ and the non-dimensional perturbed velocity $\mathbf{v}/V_0$ respectively, $p = (L_0/\rho\nu V_0)P$ the non-dimensional pressure, and ∇^2 stands for $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Three independent non-dimensional parameters are involved in the above equations, the Reynolds number $R = L_0 V_0/\nu$, the magnetic Reynolds number $R_m = \sigma\mu L_0 V_0$ and the Hartmann number $M = (\sigma/\rho\nu)^{1/2} L_0 \mu H_0 = (SRR_m)^{1/2}$ ($S = \mu H_0^2/\rho V_0^2$ being the pressure number). The equations (2.24) ~ (2.26) are identical with the Oseen equations in ordinary hydrodynamics except the terms of the Lorentz force.

Equations (2.2) and (2.4) are rewritten, by using the quantities introduced above, as

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad (2.27)$$

$$\text{and} \quad \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0, \quad (2.28)$$

respectively. Equations (2.18) and (2.19) are also rewritten in the following non-dimensional forms:

$$\left\{ \begin{aligned} \frac{\partial h^*}{\partial y} - \frac{\partial g^*}{\partial z} &= 0, \end{aligned} \right. \quad (2.29)$$

$$\left\{ \begin{aligned} \frac{\partial f^*}{\partial z} - \frac{\partial h^*}{\partial x} &= 0, \end{aligned} \right. \quad (2.30)$$

$$\left\{ \begin{aligned} \frac{\partial g^*}{\partial x} - \frac{\partial f^*}{\partial y} &= 0, \end{aligned} \right. \quad (2.31)$$

$$\text{and} \quad \frac{\partial f^*}{\partial x} + \frac{\partial g^*}{\partial y} + \frac{\partial h^*}{\partial z} = 0, \quad (2.32)$$

where (f^*, g^*, h^*) are the x, y, z -components of the non-dimensional magnetic field inside the body, $\mathbf{H}^*/H_0$.

Thus, we have obtained the set of linear equations to be solved for the present problem.

§ 3. Solution of the Linearized Equations

We shall now proceed to solve the above

linearized simultaneous equations (2.21)~(2.32). In the first place, it is easily verified that Eqs. (2.21)~(2.26) except Eq. (2.24) can be always satisfied, if we write

$$\left. \begin{aligned} f &= \frac{\partial \Phi}{\partial x} + R_m(\phi - \Phi), \\ g &= \frac{\partial \Phi}{\partial y}, \\ h &= \frac{\partial \Phi}{\partial z}, \end{aligned} \right\} \quad (3.1)$$

and

$$\left. \begin{aligned} p &= p_0 + (\nabla^2 - R \frac{\partial}{\partial x} - M^2) \phi + M^2 \Phi, \\ v &= \frac{\partial \phi}{\partial y}, \\ w &= \frac{\partial \phi}{\partial z}, \end{aligned} \right\} \quad (3.2)$$

where Φ and ϕ are functions of x , y and z , the constant p_0 being the static pressure at infinity. Now, we should search for equations to which Φ and ϕ are to be subject, and at the same time we should express u in terms of ϕ . They will be obtained from the remaining fundamental equations (2.24), (2.27) and (2.28).

Inserting (3.1) into (2.28), we have an equation for Φ and ϕ ,

$$\left(\nabla^2 - R_m \frac{\partial}{\partial x} \right) \Phi = -R_m \frac{\partial \phi}{\partial x}. \quad (3.3)$$

On the other hand, substitution of (3.2) into (2.24) and (2.27) yields

$$\left(\nabla^2 - R \frac{\partial}{\partial x} \right) u = \left(\nabla^2 - R \frac{\partial}{\partial x} - M^2 \right) \frac{\partial \phi}{\partial x} + M^2 \frac{\partial \Phi}{\partial x}, \quad (3.4)$$

$$\text{and} \quad \frac{\partial u}{\partial x} = - \left(\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) = - \left(\nabla^2 - \frac{\partial^2}{\partial x^2} \right) \phi, \quad (3.5)$$

respectively. Eliminating u from (3.4) and (3.5), we have another equation for Φ and ϕ ,

$$\left(\nabla^4 - R \nabla^2 \frac{\partial}{\partial x} - M^2 \frac{\partial^2}{\partial x^2} \right) \phi = -M^2 \frac{\partial^2 \Phi}{\partial x^2}, \quad (3.6)$$

Elimination of Φ from (3.3) and (3.6) yields the equation for Φ :

$$\left\{ \nabla^4 - (R + R_m) \nabla^2 \frac{\partial}{\partial x} - (M^2 - R R_m) \frac{\partial^2}{\partial x^2} \right\} \nabla^2 \Phi = 0. \quad (3.7)$$

Similar elimination of Φ yields the equation for ϕ :

$$\left\{ \nabla^4 - (R + R_m) \nabla^2 \frac{\partial}{\partial x} - (M^2 - R R_m) \frac{\partial^2}{\partial x^2} \right\} \nabla^2 \phi = 0, \quad (3.8)$$

which is identical with Eq. (3.7) for Φ . Eq. (3.7) can be transformed into

$$\left(\nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) \left(\nabla^2 - 2k_2 \frac{\partial}{\partial x} \right) \nabla^2 \Phi = 0, \quad (3.9)$$

where

$$k_1 = \frac{1}{4} \{ (R + R_m) + \sqrt{(R + R_m)^2 + 4(M^2 - R R_m)} \}, \quad (3.10)$$

$$k_2 = \frac{1}{4} \{ (R + R_m) - \sqrt{(R + R_m)^2 + 4(M^2 - R R_m)} \}. \quad (3.11)$$

k_2 is negative, zero or positive according as the pressure number S is larger than, equal to or smaller than unity, since the term $(M^2 - R R_m)$ in (3.11) is expressed as

$$(M^2 - R R_m) = R R_m (S - 1), \quad (3.12)$$

while k_1 is always positive except a trivial case in which $R = R_m = 0$.

In general, the solution for Eq. (3.9) can be expressed as

$$\Phi = \frac{1}{2k_1} \Phi_1 + \frac{1}{2k_2} \Phi_2 + \Phi_3, \quad (3.13)$$

where Φ_1 , Φ_2 and Φ_3 are the solutions of the following equations:

$$\left. \begin{aligned} \left(\nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) \Phi_1 &= 0, \\ \left(\nabla^2 - 2k_2 \frac{\partial}{\partial x} \right) \Phi_2 &= 0, \end{aligned} \right\} \quad (3.14)$$

$$\text{and} \quad \nabla^2 \Phi_3 = 0,$$

respectively. Inserting (3.13) into (3.3) and integrating with respect to x with the aid of (3.14), we have ϕ in the following form:

$$\phi = \frac{1}{2k_1} \phi_1 + \frac{1}{2k_2} \phi_2 + \phi_3, \quad (3.15)$$

where

$$\left. \begin{aligned} \phi_1 &= \left(1 - \frac{2k_1}{R_m} \right) \Phi_1, \\ \phi_2 &= \left(1 - \frac{2k_2}{R_m} \right) \Phi_2, \\ \phi_3 &= \Phi_3, \end{aligned} \right\} \quad (3.16)$$

and an additive arbitrary function of y and z only has been omitted from the consideration of the flow field at infinity upstream.

In like manner, substituting (3.15) into (3.5) and bearing (3.14) and (3.16) in mind, (3.5) can also be integrated with respect to x , obtaining

$$u = \frac{\partial \phi}{\partial x} - \phi_1 - \phi_2, \quad (3.17)$$

where an additive arbitrary function of y and z only has been again omitted.

The expressions for f in (3.1) and for p in (3.2) are now simplified, using (3.13), (3.14), (3.15) and (3.16), as:

$$f = \frac{\partial \Phi}{\partial x} - \Phi_1 - \Phi_2, \quad (3.18)$$

$$\text{and } p = p_0 - R \frac{\partial \phi}{\partial x} + \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial x} + M^2(\Phi - \phi). \quad (3.19)$$

We have thus obtained the formal solutions for Eqs. (2.21)~(2.28) for the field outside the body, writing them here in order,

$$\left. \begin{aligned} f &= \frac{\partial \Phi}{\partial x} - \Phi_1 - \Phi_2, \\ g &= \frac{\partial \Phi}{\partial y}, \\ h &= \frac{\partial \Phi}{\partial z}, \end{aligned} \right\} \quad (3.20)$$

$$\left. \begin{aligned} u &= \frac{\partial \phi}{\partial x} - \phi_1 - \phi_2, \\ v &= \frac{\partial \phi}{\partial y}, \\ w &= \frac{\partial \phi}{\partial z}, \end{aligned} \right\} \quad (3.21)$$

$$p = p_0 - R \frac{\partial \phi}{\partial x} + \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial x} + M^2(\Phi - \phi). \quad (3.19)$$

Denoting the x , y and z -components of the non-dimensional vorticity by ξ , η and ζ respectively, they can be expressed in terms of ϕ_1 and ϕ_2 , as follows:

$$\left. \begin{aligned} \xi &= \frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} = 0, \\ \eta &= \frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} = -\frac{\partial \phi_1}{\partial z} - \frac{\partial \phi_2}{\partial z}, \\ \zeta &= \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} = \frac{\partial \phi_1}{\partial y} + \frac{\partial \phi_2}{\partial y}. \end{aligned} \right\} \quad (3.22)$$

In like manner, the x , y and z -components of the non-dimensional current density, j_x , j_y and j_z respectively, can also be expressed as:

$$\left. \begin{aligned} j_x &= \frac{\partial h}{\partial y} - \frac{\partial g}{\partial z} = 0, \\ j_y &= \frac{\partial f}{\partial z} - \frac{\partial h}{\partial x} = -\frac{\partial \Phi_1}{\partial z} - \frac{\partial \Phi_2}{\partial z}, \\ j_z &= \frac{\partial g}{\partial x} - \frac{\partial f}{\partial y} = \frac{\partial \Phi_1}{\partial y} + \frac{\partial \Phi_2}{\partial y}. \end{aligned} \right\} \quad (3.23)$$

We shall now proceed to solve the equations in (3.14). The first and the second equations

in (3.14) are already familiar to us in the usual Oseen approximation⁵⁾. Hence, the appropriate general solution for Φ_1 can be given by

$$\Phi_1 = e^{k_1 x} \sum_{n=0}^{\infty} A_n X_n(k_1 r) S_n(\theta, \varphi), \quad (3.24)$$

$$\text{where } X_n(x) = (2n+1) \sqrt{\frac{\pi}{2x}} K_{n+\frac{1}{2}}(x), \quad (3.25)$$

$S_n(\theta, \varphi)$ a surface harmonic of degree n , A_n 's arbitrary constants of integration, K_s the modified Bessel function of the second kind, and (r, θ, φ) are the variables referring to the spherical polar coordinates with the x -axis as initial line. In like manner, the appropriate general solution for Φ_2 is given by

$$\Phi_2 = e^{k_2 x} \sum_{n=0}^{\infty} B_n X_n(|k_2| r) S_n(\theta, \varphi), \quad (3.26)$$

where B_n 's are arbitrary constants of integration, $|k_2|$ being the absolute value of k_2 . As has been shown in (3.11) and (3.12), k_2 is positive or negative according as the pressure number S is smaller or larger than unity. In order that the solution vanishes at infinity, we must take the absolute value of k_2 in the argument of the X_n 's.

The third solution Φ_3 in (3.14) is to be a harmonic function vanishing at infinity and is given by

$$\Phi_3 = \sum_{n=0}^{\infty} \frac{C_n}{r^{n+1}} S_n(\theta, \varphi), \quad (3.27)$$

where C_n 's are arbitrary constants of integration.

Equations (2.29)~(2.32) for the magnetic field inside the body can easily be solved as follows. From Eqs. (2.29)~(2.31) the magnetic field is to have a potential function, Φ^* say, such that

$$\left. \begin{aligned} f^* &= \frac{\partial \Phi^*}{\partial x}, \\ g^* &= \frac{\partial \Phi^*}{\partial y}, \\ h^* &= \frac{\partial \Phi^*}{\partial z}. \end{aligned} \right\} \quad (3.28)$$

Then, we have from (2.32),

$$\nabla^2 \Phi^* = 0. \quad (3.29)$$

Hence, Φ^* must be a harmonic function analytic at the origin and is given by

$$\Phi^* = \sum_{n=0}^{\infty} D_n r^n S_n(\theta, \varphi), \quad (3.30)$$

where D_n 's are arbitrary constants of integration.

Thus, we have obtained the general solutions for Φ_1 , Φ_2 , Φ_3 and Φ^* . The arbitrary constants of integration involved in these general solutions should be determined by the boundary conditions (2.15), (2.16) and (2.17).

The simplest example of the present problem is the flow past a sphere. Since the field is, then, axially symmetric, the surface harmonic $S_n(\theta, \varphi)$ in Φ_1 , Φ_2 , Φ_3 and Φ^* is independent of φ and is reduced to the Legendre function $P_n(\cos \theta)$. Further detailed calculations can easily be carried out, but it is more convenient to use the stream function and the magnetic stream function for the axially symmetric field than to use the present ϕ and Φ . Indeed, Gotoh carries out the detailed calculations in the subsequent paper³⁾, using the stream function and the magnetic stream function.

As for the two-dimensional case, it will be dealt with separately in later sections, since general solutions for Φ_1 , Φ_2 , Φ_3 and Φ^* will be given in somewhat different forms from the present (3.24), (3.26), (3.27) and (3.30).

§ 4. Asymptotic Behaviours of the Field

The present approximation is obviously not appropriate in the immediate neighbourhood of the body, since the perturbed velocity there becomes of the same order as the velocity of the free stream, as in the case of the Oseen approximation in ordinary hydrodynamics. However, it will give a fairly good asymptotic behaviours of the field at large distances from the body.

Since, for large values of $k_1 r$, the modified Bessel function $K_{n+\frac{1}{2}}(k_1 r)$ has the asymptotic expression:

$$K_{n+\frac{1}{2}}(k_1 r) \sim \left(\frac{\pi}{2k_1 r} \right)^{\frac{1}{2}} e^{-k_1 r}, \quad (4.1)$$

all the fundamental solutions in Φ_1 presented in (3.24) are of the order of

$$\left(\frac{\pi}{2k_1 r} \right)^{\frac{1}{2}} e^{-k_1(r-x)}. \quad (4.2)$$

Hence, they fall off exponentially when r tends to ∞ , except within a region bounded more or less vaguely by a paraboloidal surface expressed by

$$\begin{aligned} & k_1(r-x) = c, \\ \text{or} \quad & y^2 + z^2 = \frac{2c}{k_1} x + \frac{c^2}{k_1^2}, \end{aligned} \quad (4.3)$$

where c is a certain positive constant of $O(1)$. This paraboloid has its focus at the origin of the coordinates and its axis of symmetry along the x -axis, and is open in the positive x -direction, since k_1 is always positive.

In like manner, all the fundamental solutions in Φ_2 presented in (3.26) are sensible only within a region bounded by a paraboloidal surface expressed by

$$\begin{aligned} & k_2(r-x) = c, \quad (\text{for } k_2 > 0) \\ & -k_2(r+x) = c, \quad (\text{for } k_2 < 0) \\ \text{or} \quad & y^2 + z^2 = \frac{2c}{k_2} x + \frac{c^2}{k_2^2}. \end{aligned} \quad (4.4)$$

This paraboloid is similar to the preceding one, but is open in the positive or negative x -direction according as k_2 is positive or negative, or according as the pressure number S is smaller or larger than unity.

Thus, it is easily found from (3.22) and (3.23) that rotational field with appreciable vortices and induced currents is confined within the two paraboloidal regions, outside which the field is almost irrotational. The structure of the rotational field is closely similar to that of the wake in the classical Oseen flow. However, in the present case, the two rotational regions are formed in couples, while the single wake is formed behind the body in the classical Oseen flow.

Now, remembering (4.3) and (4.4), we can attain an interesting conclusion that there may be three distinct types of the field. When $S > 1$, the two paraboloidal rotational regions are formed so that one in front and the other in rear of the body. When $S < 1$, on the other hand, they are doubly formed in rear of the body. For the transitional value of $S = 1$, i.e. $k_2 = 0$, it is found from (3.26) that the rotational field associated with Φ_2 extends over the whole field, while that associated with Φ_1 is still confined within a paraboloidal region formed behind the body. It is also found from (3.22) and (3.23) that the vorticity and the current density associated with Φ_2 fall off not exponentially but only as r^{-2} when r tends to ∞ .

These facts are quite due to the existence of the magnetic field. Roughly speaking, in the ordinary hydrodynamic flow, the vortices produced at the surface of the body are diffused in all directions by the viscosity and swept away down-stream by the main stream. Thus, the vortices are mostly confined in the

paraboloidal region behind the body and are hardly transferred upstream. In the present case, however, owing to the existence of the magnetic field the disturbances in velocity caused by the body are transmitted along the lines of magnetic force, as the so-called Alfvén waves. The present Φ_1 implies the disturbances transmitted by the waves travelling in the positive x -direction, while Φ_2 implies the disturbances transmitted by the waves which would travel in the negative x -direction essentially. The vortices are now transferred through three ways: diffusion in all directions by viscosity, convection downstream by the main stream and the above-mentioned transmission along the lines of magnetic force as the Alfvén waves.

Hence, it is important for determining the type of the field whether the velocity of the main stream is greater or smaller than that of the transmission of the Alfvén waves. Since the velocity of the Alfvén waves a is given by†

$$a = H\sqrt{\mu/\rho}, \quad (4.5)$$

the pressure number S can be interpreted as the square of the ratio of the characteristic wave velocity to the characteristic stream velocity, viz.

$$S = \left(\frac{a_0}{V_0} \right)^2, \quad (a_0 = H_0\sqrt{\mu/\rho}) \quad (4.6)$$

though it has been defined in §2 as the ratio of the characteristic magnetic pressure to the characteristic dynamic pressure.

Since, for $S > 1$, the effect of the transmission dominates that of the convection, the vortices are transferred upstream as well as downstream. The effect of the diffusion by viscosity tends to expand the rotational regions in the normal directions to the stream. Thus, in front and in rear of the body are formed the two paraboloidal rotational regions extending broader upstream and downstream respectively.

For $S < 1$, on the other hand, the effect of the convection dominates that of the transmission, so that even the disturbances associated with Φ_2 are swept away downstream. Hence, the disturbances are hardly transferred upstream and the paraboloidal rotational regions are doubly formed in rear of the body.

† See, e.g., T. G. Cowling: *Magnetohydrodynamics* (Interscience Publishers, 1957) Chapter 3.

In general, it can be said that the paraboloid associated with Φ_2 extends broader than that associated with Φ_1 , since the transmission upstream is decelerated by the effect of convection while that downstream is accelerated. This is shown in the fact that the absolute value of k_2 is always smaller than k_1 .

For $S=1$, the disturbances associated with Φ_2 are now only diffused by viscosity, since the effects of the convection and of the transmission cancel out each other. Hence, the rotational region associated with Φ_2 extends over the whole field.

Thus, $S^{-\frac{1}{2}} = V_0/a_0$ has a certain analogy with the Mach number in ordinary hydrodynamics of a compressible fluid. The flows for $S > 1$, $S=1$ and $S < 1$ correspond respectively to the subsonic, the sonic and the supersonic flows. In reality, however, since the present fluid has a finite kinematic viscosity ν and a finite magnetic viscosity $1/\sigma\mu$, the boundaries of the paraboloidal regions are not distinct and the

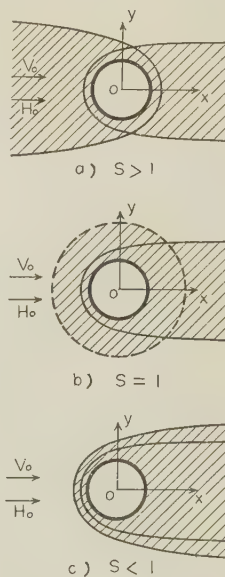


Fig. 1. Schematic diagrams of the rotational regions.

rotational region extends a little ahead of the body even for the 'supersonic' flow.

The rotational regions in the magnetic field, where the appreciable electric currents are induced, will also be formed in accordance with the above-mentioned vortex regions, since in the Alfvén waves the disturbances in velocity are always accompanied by those in

magnetic field. Indeed, in the present case, this is exactly shown in the fact that the both fields are expressed in linear combinations of the three functions Φ_1 , Φ_2 and Φ_3 .

The three distinct types of the field are roughly illustrated in Fig. 1, where the shadowed regions express the rotational regions.

§ 5. Solution for the Two-dimensional Flow

We shall now consider the flow past a cylinder set at right angles to the undisturbed flow. Taking the z -axis parallel to the generator of the cylinder, we can omit Eqs. (2.21), (2.22), (2.26), (2.29) and (2.30) from the set of the linearized governing equations (2.21) ~ (2.32), and can also omit the derivatives with respect to z involved there.

The general solution can be obtained by a similar procedure to that developed in § 3. However, for the two-dimensional field, it is more convenient to introduce a stream function ϕ and a magnetic stream function Ψ such that

$$\left. \begin{aligned} u &= -\frac{\partial \phi}{\partial y}, \\ v &= \frac{\partial \phi}{\partial x}, \end{aligned} \right\} \quad (5.1)$$

and

$$\left. \begin{aligned} f &= -\frac{\partial \Psi}{\partial y}, \\ g &= \frac{\partial \Psi}{\partial x}, \end{aligned} \right\} \quad (5.2)$$

respectively. Then, Eqs. (2.27) and (2.28) without the third terms are readily satisfied. Eliminating p from Eqs. (2.24) and (2.25), we have the same equation as Eq. (3.6):

$$\left(\nabla^4 - R \nabla^2 \frac{\partial}{\partial x} - M^2 \frac{\partial^2}{\partial x^2} \right) \phi = -M^2 \frac{\partial^2 \Psi}{\partial x^2}, \quad (5.3)$$

∇^2 standing here for the two-dimensional Laplacian $\partial^2/\partial x^2 + \partial^2/\partial y^2$. Equation (2.23) are also written in terms of Ψ and ϕ as:

$$\left(\nabla^2 - R_m \frac{\partial}{\partial x} \right) \Psi = -R_m \frac{\partial \phi}{\partial x}, \quad (5.4)$$

which is also the same as Eq. (3.3).

Elimination of ϕ or Ψ from Eqs. (5.3) and (5.4) yields a single identical equation for Ψ or ϕ :

$$\left\{ \nabla^4 - (R + R_m) \nabla^2 \frac{\partial}{\partial x} + (RR_m - M^2) \frac{\partial^2}{\partial x^2} \right\} \nabla^2(\Psi, \phi) = 0, \quad (5.5)$$

which is also the same as the equations (3.7) for Φ and (3.8) for ϕ .

Solution of (5.5) can be given in the same way as has been done in solving (3.7) and (3.8). Hence, we have

$$\Psi = \Psi_1 + \Psi_2 + \Psi_3, \quad (5.6)$$

and

$$\phi = \left(1 - \frac{2k_1}{R_m} \right) \Psi_1 + \left(1 - \frac{2k_2}{R_m} \right) \Psi_2 + \Psi_3, \quad (5.7)$$

where Ψ_1 , Ψ_2 and Ψ_3 are the solutions of the following equations:

$$\left. \begin{aligned} \left(\nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) \Psi_1 &= 0, \\ \left(\nabla^2 - 2k_2 \frac{\partial}{\partial x} \right) \Psi_2 &= 0, \end{aligned} \right\} \quad (5.8)$$

and $\nabla^2 \Psi_3 = 0$,

where k_1 and k_2 are identical with those in (3.10) and (3.11) respectively.

The pressure p is obtained by integrating (2.24) and (2.25). Thus,

$$p = p_0 + (R - 2k_1) \frac{\partial \phi_1}{\partial y} + (R - 2k_2) \frac{\partial \phi_2}{\partial y} + R \frac{\partial \phi_3}{\partial y}, \quad (5.9)$$

$$\left. \begin{aligned} \text{where } \phi_1 &= \left(1 - \frac{2k_1}{R_m} \right) \Psi_1, \\ \phi_2 &= \left(1 - \frac{2k_2}{R_m} \right) \Psi_2, \end{aligned} \right\} \quad (5.10)$$

and $\phi_3 = \Psi_3$.

The vorticity and the current density are also expressed as

$$\zeta = \nabla^2 \phi = 2k_1 \frac{\partial \phi_1}{\partial x} + 2k_2 \frac{\partial \phi_2}{\partial x}, \quad (5.11)$$

and

$$j_z = \nabla^2 \Psi = 2k_1 \frac{\partial \Psi_1}{\partial x} + 2k_2 \frac{\partial \Psi_2}{\partial x}. \quad (5.12)$$

Introducing the magnetic stream function Ψ^* inside the cylinder, Eq. (2.31) is reduced to

$$\nabla^2 \Psi^* = 0. \quad (5.13)$$

The first and the second equations in (5.8) are already familiar to us in the ordinary Oseen flow, whose general solution was given by Filon⁹⁾. Following Filon, we get Ψ_1 in the form:

$$\begin{aligned} \Psi_1 &= A_0 e^{k_1 x} K_0(k_1 r) \\ &+ B_0 \int_0^\theta k_1 r [K_1(k_1 r) + K_0(k_1 r) \cos \chi] e^{k_1 r \cos \chi} d\chi \\ &+ 2e^{k_1 x} \sum_{n=1}^{\infty} K_n(k_1 r) (A_n \cos n\theta + B_n \sin n\theta), \end{aligned} \quad (5.14)$$

where $x = r \cos \theta$, $y = r \sin \theta$ and K_n denotes the modified Bessel function of the second

kind, A_n 's and B_n 's being arbitrary constants of integration.

As for Ψ_2 , we must remember that k_2 is positive or negative according as the pressure number S is smaller or larger than unity. For $k_2 > 0$, Ψ_2 will be expressed in the form similar to that of the above Ψ_1 . For $k_2 < 0$, on the other hand, it will be expressed in the form similar to that of the second stream function in our previous paper²⁾. Hence, Ψ_2 is given by

$$\begin{aligned} \Psi_2 = & C_0 e^{k_2 x} K_0(|k_2|r) \\ & + D_0 \int_0^\theta |k_2|r [K_1(|k_2|r) \pm K_0(|k_2|r) \cos \chi] e^{k_2 r \cos \chi} d\chi \\ & + 2e^{k_2 x} \sum_{n=1}^{\infty} K_n(|k_2|r) (C_n \cos n\theta + D_n \sin n\theta), \end{aligned} \quad (5.15)$$

where, in the second term multiplied by D_0 , the plus and minus signs correspond to $k_2 > 0$ and $k_2 < 0$ respectively, and C_n 's and D_n 's are arbitrary constants of integration.

The third equation in (5.8) shows that Ψ_3 must be a harmonic function. Hence, we have the appropriate general solution for Ψ_3 as:

$$\Psi_3 = a_0 \ln r + b_0 \theta + \sum_{n=1}^{\infty} r^{-n} (a_n \cos n\theta + b_n \sin n\theta), \quad (5.16)$$

where a_n 's and b_n 's are arbitrary constants of integration.

In like manner, Ψ^* must be a harmonic function analytic at the origin. Thus, we have

$$\Psi^* = a_0^* + \sum_{n=1}^{\infty} r^n (a_n^* \cos n\theta + b_n^* \sin n\theta), \quad (5.17)$$

where a_n^* 's and b_n^* 's are arbitrary constants of integration.

As was shown by Filon⁶⁾ in the classical Oseen flow, the terms multiplied by B_0 in the expression for Ψ_1 and by D_0 in that for Ψ_2 contain non-periodic terms in θ and may be expanded as:

$$\begin{aligned} & \int_0^\theta |k|r [K_1(|k|r) \pm K_0(|k|r) \cos \chi] e^{k r \cos \chi} d\chi \\ & = \theta + \text{periodic terms in } \theta, \end{aligned} \quad (5.18)$$

where k stands for k_1 in Ψ_1 and for k_2 in Ψ_2 respectively. These many-valuednesses of Ψ_1 and Ψ_2 should be cancelled out by adding the third many-valued fundamental solution θ in Ψ_3 , since both the magnetic stream function Ψ and the ordinary stream function ϕ must be one-valued. Hence, the following conditions

should be imposed on the constants B_0 , D_0 and b_0 : for the one-valuedness of the magnetic stream function Ψ ,

$$B_0 + D_0 + b_0 = 0, \quad (5.19)$$

and for the one-valuedness of the ordinary stream function ϕ ,

$$\left(1 - \frac{2k_1}{R_m}\right) B_0 + \left(1 - \frac{2k_2}{R_m}\right) D_0 + b_0 = 0, \quad (5.20)$$

or, combining this with (5.19),

$$k_1 B_0 + k_2 D_0 = 0. \quad (5.21)$$

Thus, we have obtained the general solutions for Ψ and Ψ^* . We shall next consider the asymptotic behaviours of the field from the general solutions obtained above. Since, for large values of $|k|r$, the modified Bessel function $K_n(|k|r)$ has the asymptotic expression:

$$K_n(|k|r) \sim \left(\frac{\pi}{2|k|r}\right)^{\frac{1}{2}} e^{-|k|r}, \quad (5.22)$$

Ψ_1 and Ψ_2 are only sensible within the regions bounded by the surfaces of parabolic cylinders expressed by

$$y^2 = \frac{2c}{k_1} x + \frac{c^2}{k_1^2}, \quad (5.23)$$

$$\text{and } y^2 = \frac{2c}{k_2} x + \frac{c^2}{k_2^2}, \quad (5.24)$$

respectively. Hence, it is found from (5.11) and (5.12) that rotational field with appreciable vortices and induced currents is also confined within the two cylindrical parabolic regions, outside which the field is almost irrotational. The state of affairs is quite the same as that mentioned in the last section for the three-dimensional flow.

As an example of the two-dimensional flow, we shall now consider the flow past a circular cylinder. The arbitrary constants involved in the general solutions for Ψ and Ψ^* should be determined by the boundary conditions appropriate for the present problem.

The boundary conditions at infinity (2.15) are already satisfied by Ψ and ϕ obtained above. Taking the origin of the coordinates at the centre of the cylinder, the field is symmetrical with respect to the x -axis. This implies that all the constants A_n 's, C_n 's, a_n 's and a_n^* 's must be zero. The remaining constants B_n 's, D_n 's, b_n 's and b_n^* 's are now to be determined from the boundary conditions at the surface of the cylinder, (2.16) and (2.17), which are now expressed as

$$\left. \begin{aligned} \cos \theta + v_r &= 0, \\ -\sin \theta + v_\theta &= 0, \end{aligned} \right\} \quad \text{at } r=1, \quad (5.25)$$

length L_0 , and the subscripts r and θ denote the components of the vector quantities in the directions of r increasing and θ increasing respectively.

Since the respective components of the velocity and the magnetic field can be written in terms of Ψ_1, Ψ_2, Ψ_3 and Ψ^* , Eqs. (5.25) and (5.26) can be expressed as:

$$\left. \begin{aligned} \mu(\cos \theta + h_r) - \mu^* h_r^*, \\ -\sin \theta + h_\theta = h_\theta^*, \end{aligned} \right\} \quad \text{at } r=1, \quad (5.26)$$

respectively, where the radius of the circular cylinder has been taken as a characteristic

$$\left. \begin{aligned} \cos \theta - \left\{ \left(1 - \frac{2k_1}{R_m}\right) \frac{\partial \Psi_1}{\partial \theta} + \left(1 - \frac{2k_2}{R_m}\right) \frac{\partial \Psi_2}{\partial \theta} + \frac{\partial \Psi_3}{\partial \theta} \right\}_{r=1} &= 0, \\ \sin \theta - \left\{ \left(1 - \frac{2k_1}{R_m}\right) \frac{\partial \Psi_1}{\partial r} + \left(1 - \frac{2k_2}{R_m}\right) \frac{\partial \Psi_2}{\partial r} + \frac{\partial \Psi_3}{\partial r} \right\}_{r=1} &= 0, \end{aligned} \right\} \quad (5.27)$$

and

$$\left. \begin{aligned} \kappa \left\{ \cos \theta - \left(\frac{\partial \Psi_1}{\partial \theta} + \frac{\partial \Psi_2}{\partial \theta} + \frac{\partial \Psi_3}{\partial \theta} \right)_{r=1} \right\} &= - \left(\frac{\partial \Psi^*}{\partial \theta} \right)_{r=1}, \\ \sin \theta - \left(\frac{\partial \Psi_1}{\partial r} + \frac{\partial \Psi_2}{\partial r} + \frac{\partial \Psi_3}{\partial r} \right)_{r=1} &= - \left(\frac{\partial \Psi^*}{\partial r} \right)_{r=1}, \end{aligned} \right\} \quad (5.28)$$

respectively, where $\kappa = \mu/\mu^*$. These four equations are now to be satisfied independently of θ . In place of (5.28) we may take the following simpler equations:

$$\left. \begin{aligned} \frac{2\kappa}{R_m} \left(k_1 \frac{\partial \Psi_1}{\partial \theta} + k_2 \frac{\partial \Psi_2}{\partial \theta} \right)_{r=1} &= \left(\frac{\partial \Psi^*}{\partial \theta} \right)_{r=1}, \\ \frac{2}{R_m} \left(k_1 \frac{\partial \Psi_1}{\partial r} + k_2 \frac{\partial \Psi_2}{\partial r} \right)_{r=1} &= \left(\frac{\partial \Psi^*}{\partial r} \right)_{r=1}, \end{aligned} \right\} \quad (5.29)$$

which are obtained by eliminating the terms $(\partial \Psi_3 / \partial \theta)_{r=1}$ and $(\partial \Psi_3 / \partial r)_{r=1}$ from (5.27) and (5.28).

Making use of the following relations,[†]

$$e^{ik \cos \theta} \left\{ \begin{aligned} \cos n\theta \\ \sin n\theta \end{aligned} \right\} = \left\{ \begin{aligned} I_n(k) + \sum_{m=1}^{\infty} \{I_{n-m}(k) + I_{n+m}(k)\} \cos m\theta, \\ \sum_{m=1}^{\infty} \{I_{n-m}(k) - I_{n+m}(k)\} \sin m\theta, \end{aligned} \right\} \quad (5.30)$$

we expand the both sides of the four equations in (5.27) and (5.29) in Fourier series. Then, equating the coefficients of $\cos m\theta$ and $\sin m\theta$ on both sides of each equation, we get four sets of simultaneous algebraic equations for determining the constants B_n 's, D_n 's, b_n 's and b_n^* 's. For simplicity's sake, these rather lengthy equations will not be reproduced here, but it is to be remarked that the necessary conditions (5.19) and (5.20) for one-valuedness of Ψ and ϕ are ascertained by these algebraic equations. The constants B_n 's, D_n 's, b_n 's and b_n^* 's may be expressed, in principle, in terms of the four independent parameters k_1, k_2, R_m and κ , contained in the algebraic equations, but it is hardly possible to get them exactly.

The present perturbation method of solution fails to approximate the real field in the immediate neighbourhood of the body, as has been mentioned at the beginning of § 4. However this defect will not be so serious for the flow at small Reynolds and magnetic Reynolds numbers, as is well known in the ordinary Oseen approximation. Now, we suppose that R and R_m , and hence also k_1 and k_2 , are of small values of the order ϵ , while κ is of the order

[†] Here we make use of the fact that when s is any positive integer, the modified Bessel function of the first kind $I_s(x)$ can be expressed as:

$$I_s(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{x \cos \theta} \cos s\theta \, d\theta.$$

of unity, which is the case for usual materials. Then, we can obtain the constants B_n 's, D_n 's, b_n 's and b_n^* 's in powers of ϵ . To the lowest order of ϵ , we have

$$B_0 = \frac{2R_m}{k_1[(R_m - 2k_1)\{1 + 2\mathcal{Q}(k_1)\} - (R_m - 2k_2)\{1 + 2\mathcal{Q}(|k_2|)\}]} , \quad (5.31)$$

$$D_0 = - \frac{2R_m}{k_2[(R_m - 2k_1)\{1 + 2\mathcal{Q}(k_1)\} - (R_m - 2k_2)\{1 + 2\mathcal{Q}(|k_2|)\}]} , \quad (5.32)$$

and

$$b_0 = \frac{2R_m(k_1 - k_2)}{k_1 k_2 [(R_m - 2k_1)\{1 + 2\mathcal{Q}(k_1)\} - (R_m - 2k_2)\{1 + 2\mathcal{Q}(|k_2|)\}]} , \quad (5.33)$$

where $\mathcal{Q}(k) = -(\gamma + \ln(k/2))$, $\gamma = 0.57721 \dots$ being Euler's constant. The parameter κ does not appear to this order of approximation, but comes into the next higher orders.

About $S=1$, i.e. $k_2=0$, they behave as

$$B_0 \sim \frac{1}{k_1 \ln k_2} , \quad (5.34)$$

$$D_0 \sim - \frac{1}{k_2 \ln k_2} , \quad (5.35)$$

and

$$b_0 \sim \frac{1}{k_2 \ln k_2} , \quad (5.36)$$

respectively. Hence, it is easily found that we cannot give an appropriate solution for the transitional case $S=1$, since the above D_0 and b_0 tend to ∞ while B_0 to 0, as $S \rightarrow 1$. On the other hand, it is shown in the subsequent paper by Gotoh³⁾ that using the present perturbation method, a plausible solution can be given for the flow past a sphere even at $S=1$. The present state of affairs at $S=1$ is quite similar to that in the classical Stokes flows.

§ 6. Forces on the Cylinder

Next, we shall calculate the forces experienced by the cylinder. They can be calculated by extending the usual method in ordinary hydrodynamics. In the magnetohydrodynamic problems, however, contributions to the forces come from the Maxwell stress as well as from the usual viscous stress.

Take a contour C in the xy -plane everywhere at great distances from the cylinder. Let X' and Y' be the x - and y -components of the non-dimensional force $\mathbf{F}'/\rho\nu V_0$ exerted by the fluid outside C on the fluid of unit thickness inside, and X and Y the x - and y -components of the non-dimensional force $\mathbf{F}/\rho\nu V_0$ exerted by the surrounding fluid on the unit span of the cylinder. Then, $X' - X$ must be equal to the x -component of the rate of outflow of momentum through C , G_x say, since we are now considering the steady state only. Hence, we have

$$X = X' - G_x . \quad (6.1)$$

In the present case, X' is expressed in terms of the usual viscous stress and Maxwell's magnetic stress, as:

$$\begin{aligned} X' &= \int_C \left\{ \left(-p + 2 \frac{\partial u}{\partial x} \right) l + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) m \right\} dC + SR \int_C \left[\frac{1}{2} \{ (1+f)^2 - g^2 \} l + (1+f)gm \right] dC \\ &= \int_C (-pl - \xi m) dC + 2 \int_C \left(\frac{\partial u}{\partial x} l + \frac{\partial v}{\partial x} m \right) dC \\ &\quad + SR \int_C \frac{1}{2} l dC + SR \int_C (fl + gm) dC + SR \int_C \left\{ \left(\frac{1}{2} f^2 - g^2 \right) l + fgm \right\} dC , \end{aligned} \quad (6.2)$$

where dC is the line-element of the contour C and integrations are taken round the contour, l and m the direction-cosines of the outward normal to C .

In the first place, using the equation of continuity, the second integral in the second line of (6.2) can be written in the form:

$$\int_{\sigma} \left(\frac{\partial u}{\partial x} l + \frac{\partial v}{\partial x} m \right) dC = \int_{\sigma} \left(-\frac{\partial v}{\partial y} l + \frac{\partial v}{\partial x} m \right) dC = - \int_{\sigma} \frac{\partial v}{\partial C} dC, \quad (6.3)$$

where $\partial/\partial C$ denotes the partial differentiation along the contour C . Since v is the one-valued function, this integral must vanish. Obviously the first integral in the last line of (6.2) vanishes identically. Next, it can be seen from the asymptotic behaviours of Ψ_1 , Ψ_2 and Ψ_3 that the perturbed magnetic field is of the order of r^{-1} outside the parabolic regions mentioned in the last section and is of the order of $r^{-\frac{1}{2}}$ within, but the angles subtended by the portion of C within the regions are of the order of $r^{-\frac{1}{2}}$. Hence, the last integral in (6.2) vanishes in the limit of $r \rightarrow \infty$.

On the other hand, G_x is expressed in the form:

$$\begin{aligned} G_x &= R \int_{\sigma} \{ (1+u)l + vm \} (1+u) dC \\ &= R \int_{\sigma} l dC + R \int_{\sigma} (2ul + vm) dC + R \int_{\sigma} (u^2 l + uvm) dC. \end{aligned} \quad (6.4)$$

The first and the third integrals in the second line of the above equation vanish likewise.

Thus, we have

$$X = \int_{\sigma} (-pl - \xi m) dC + SR \int_{\sigma} (fl + gm) dC - R \int_{\sigma} (2ul + vm) dC. \quad (6.5)$$

Substituting (5.1), (5.2), (5.9) and (5.11) into these integrands, we have, after some calculations,

$$\begin{aligned} X &= \int_{\sigma} \frac{\partial}{\partial C} (2k_1 \phi_1 + 2k_2 \phi_2 - SR\Psi + R\phi) dC \\ &= \int_{\sigma} \frac{\partial}{\partial C} (2k_1 \phi_1 + 2k_2 \phi_2 + SR\Psi - R\phi) dC - 2 \int_{\sigma} \frac{\partial}{\partial C} (SR\Psi - R\phi) dC. \end{aligned} \quad (6.6)$$

Since the stream function ϕ and the magnetic stream function Ψ are one-valued, the last integral vanishes identically. Expressing the first integral in the second line in terms of Ψ_1 , Ψ_2 and Ψ_3 , we have, after some arrangements,

$$\begin{aligned} X &= -\frac{1}{R_m} \int_{\sigma} \frac{\partial}{\partial C} \left[\{ 4k_1^2 - 2k_1(R + R_m) - (M^2 - RR_m) \} \Psi_1 \right. \\ &\quad \left. + \{ 4k_2^2 - 2k_2(R + R_m) - (M^2 - RR_m) \} \Psi_2 - (M^2 - RR_m) \Psi_3 \right] dC. \end{aligned} \quad (6.7)$$

The coefficients of Ψ_1 and Ψ_2 above are identically equal to zero on account of (3.10) and (3.11). Hence, we have

$$X = \frac{M^2 - RR_m}{R_m} \int_{\sigma} \frac{\partial \Psi_3}{\partial C} dC. \quad (6.8)$$

This integral has a finite value, since Ψ_3 is the many-valued function. Remembering (5.16), the only contribution to the integral comes from the second term $b_0\theta$ in Ψ_3 . Hence, we have

$$X = \frac{2\pi}{R_m} (M^2 - RR_m) b_0 = -\frac{8\pi}{R_m} k_1 k_2 b_0, \quad (6.9)$$

where use has been made of (3.10) and (3.11).

In like manner, Y is calculated as follows:

$$\begin{aligned} Y &= Y' - G_y \\ &= \int_{\sigma} (\xi l - pm) dC + SR \int_{\sigma} (gl - fm) dC - R \int_{\sigma} v l dC \\ &= \int_{\sigma} \frac{\partial}{\partial n} (2k_1 \phi_1 + 2k_2 \phi_2 + SR\Psi - R\phi) dC \\ &= \frac{M^2 - RR_m}{R_m} \int_{\sigma} \frac{\partial \Psi_3}{\partial n} dC, \end{aligned} \quad (6.10)$$

where $\partial/\partial n$ denotes the partial differentiation along the outward normal n to C , G_y being the y -component of the rate of outflow of momentum through C . Only contribution to the last integral comes from the first term $a_0 \ln r$ in Ψ_3 , since all the integrals of the other terms vanish in the limit of $r \rightarrow \infty$. Hence, we have

$$Y = \frac{2\pi}{R_m} (M^2 - RR_m) a_0 = -\frac{8\pi}{R_m} k_1 k_2 a_0, \quad (6.11)$$

where again use has been made of (3.10) and (3.11).

For the flow past a circular cylinder, it is obvious that the lift $L (= \rho \nu V_0 Y)$ vanishes on account of the symmetry of the field with respect to the x -axis. On the other hand, using the value of b_0 obtained in the last section, we can readily calculate an approximate formula for the drag $D (= \rho \nu V_0 X)$. Thus, inserting (5.33) into (6.9), we have

$$D = \frac{16\pi\rho\nu V_0 (k_1 - k_2)}{[(R_m - 2k_2)\{1 + 2\mathcal{Q}(|k_2|)\} - (R_m - 2k_1)\{1 + 2\mathcal{Q}(k_1)\}]} \quad (6.12)$$

As the limiting cases of the above formula, we can immediately obtain the drags for a circular cylinder in the ordinary Oseen flow and in the magnetohydrodynamic Stokes flow given in our previous paper²⁾.

(I) The case of $R_m = 0$

When the electric conductivity of the fluid σ , and hence R_m too, is supposed to be zero, there exists no current in the field and the flow does not interact with the magnetic field. Hence, the flow field is to be described in ordinary hydrodynamics. Putting $R_m = 0$ in (3.10) and (3.11), we have $k_1 = R/2$ and $k_2 = 0$, for which (6.12) is reduced to

$$D = \frac{8\pi\rho\nu V_0}{\left\{1 + 2\mathcal{Q}\left(\frac{R}{2}\right)\right\}} = \frac{4\pi\rho\nu V_0}{\frac{1}{2} - \gamma - \ln\left(\frac{R}{4}\right)}. \quad (6.13)$$

This is Lamb's well-known formula itself.

(II) The case of $S = 0$

When the magnetic field vanishes, the flow is also to be described in ordinary hydrodynamics. Putting $S = \mu H_0^2 / \rho V_0^2 = 0$ in (3.10) and (3.11), we have $k_1 = R/2$ and $k_2 = R_m/2$. Then, (6.12) is also reduced to (6.13).

(III) The case of $R = R_m = 0$ with finite M

When the velocity of the fluid is very small but the magnetic field is so strong that the Hartmann number $M = (SRR_m)^{1/2}$ is finite, the field is to be dealt with by the magnetohydrodynamic Stokes approximation proposed by Chester¹⁾. Putting $R = R_m = 0$, but retaining M to be finite in (3.10) and (3.11), we have $k_1 = M/4$ and $k_2 = -M/4$. Then, (6.12) is reduced to

$$D = \frac{8\pi\rho\nu V_0}{\left\{1 + 2\mathcal{Q}\left(\frac{M}{4}\right)\right\}} = \frac{4\pi\rho\nu V_0}{\frac{1}{2} - \gamma - \ln\left(\frac{M}{8}\right)}, \quad (6.14)$$

which coincides, to the first approximation, with what has been given in our previous paper²⁾.

The drag coefficient $C_D (= D / \rho \nu V_0)$ † is expressed in terms of the three parameters k_1 , k_2 and R_m in the present case. Since k_1 and k_2 are written in terms of R , R_m and M or S , as has been shown in (3.11) and (3.12), C_D may also be regarded as a function of R , R_m and M or S . Numerical values of C_D for various

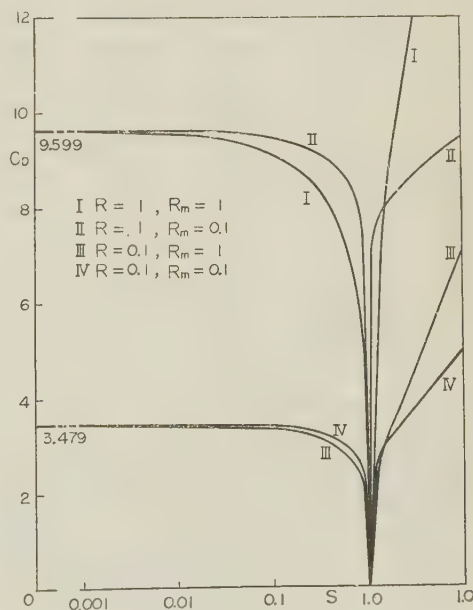


Fig. 2. Drag coefficient C_D versus S .

values of S have been computed only for the four sets of particular values of $R=0.1, 1$ and $R_m=0.1, 1$. They are tabulated in Table I and are shown graphically in Fig. 2.

† The present drag coefficient differs by the factor R from the usual one defined by $D / (\frac{1}{2} \rho V_0^2 \cdot 2L_0)$.

The numerical values of C_D , 3.479 for $R=0.1$ and 9.599 for $R=1$, on the left border line of the graph are those in the ordinary Oseen flow. The drag coefficients decrease very slowly with increase of S and then fall to 0 abruptly at $S=1$. Passing over this point, they again return to normal abruptly and then increase with S .

We can see from (6.12) that C_D behaves near the point $S=1$ as

$$C_D \sim \frac{1}{\ln|S-1|}. \tag{6.15}$$

This singularity is wholly due to the breakdown of the present perturbation method of solution at $S=1$ discussed in §5, since the real field should be regular and yield a finite drag even at $S=1$.

It may be remarked here that magneto-hydrodynamic effects, i.e. increases of S and R_m , cause the decrease of the drag when $S<1$, but the reverse is the case when $S>1$, so far as the present numerical results are concerned.

Table I. C_D for various values of S

S	$R=0.1$		$R=1$	
	$R_m=0.1$	$R_m=1$	$R_m=0.1$	$R_m=1$
0	3.479	3.479	9.599	9.599
0.001	3.479	3.479	9.598	9.597
0.01	3.475	3.471	9.583	9.562
0.1	3.429	3.397	9.469	9.118
0.5	3.155	2.976	8.841	7.590
0.8	2.845	2.520	8.146	5.945
1.0	0	0	0	0
1.2	2.845	2.499	7.683	4.055
1.5	3.175	3.107	8.005	7.590
2.0	3.479	3.710	8.275	9.599
3.0	3.849	4.535	8.626	—
5.0	4.306	5.740	9.342	—
10.	5.000	7.901	—	—
100.	8.563	—	—	—

The drag for a sphere is also calculated by Gotoh³⁾. It does not break down so seriously at $S=1$, though it has similar tendencies to those for a circular cylinder. It takes minimum but non-zero values at $S=1$. The curves for C_D are bent off there with finite jump of inclination of the tangent.

§ 7. Conclusion

An approximate method of solution similar to Oseen approximation has been proposed to

investigate the flow of a viscous, incompressible and electrically conducting fluid past a fixed body in a parallel magnetic field.

From the consideration of the asymptotic behaviours of the field at great distances from the body, it is found that the rotational field with the appreciable vortices and the induced currents is confined within the two paraboloidal regions for the three-dimensional flow, or within the two cylindrical parabolic regions for the two-dimensional flow. It is interesting that there may be three distinct types of the field according as the pressure number is greater than, equal to or smaller than unity, and that each has a certain correspondence to the subsonic, the sonic or the supersonic flow in ordinary hydrodynamics of a compressible fluid.

At $S=1$, the present perturbation method of solution fails to give an appropriate solution for the two-dimensional flow, while it gives a plausible solution for the three-dimensional flow. The state of affairs is quite similar to that in the ordinary Stokes approximation. Another method of closer approximation will be required near $S=1$, just as the transonic approximation should be in ordinary aerodynamics.

Acknowledgements

The writer wishes to express his cordial thanks to Professor S. Tomotika for his continual guidance and encouragement throughout this work, and especially for his kind inspection of the manuscript. The writer's thanks are also due to Professors I. Imai and K. Tamada for their kind advices and helpful discussions.

References

1) W. Chester: J. Fluid Mech. **3** (1957) 304.
2) H. Yosinobu and T. Kakutani: J. Phys. Soc. Japan **14** (1959) 1433.
3) K. Gotoh: J. Phys. Soc. Japan **15** (1960) 189.
4) G. K. Batchelor: Proc. Roy. Soc. A, **201** (1950) 405.
5) S. Goldstein: Proc. Roy. Soc. A, **123** (1929) 216.
6) L.N.G. Filon: Proc. Roy. Soc. A, **113** (1927) 7.

Magnetohydrodynamic Flow past a Sphere

By Kanefusa GOTOH

Department of Physics, Faculty of Science, Kyoto University

(Received August 27, 1959)

The flow of an incompressible, viscous, electrically conducting fluid past a sphere in the presence of a uniform magnetic field parallel to the undisturbed flow is investigated using Oseen approximation. The drag coefficient is calculated up to the second order of magnitudes of parameters: the Reynolds number R , the magnetic Reynolds number R_m and the Hartmann number M . Its numerical values are shown graphically for a few typical cases. It is found that the drag coefficient is continuous at the pressure number $S=1$, whereas it changes there abruptly in the two-dimensional case. The flow pattern changes remarkably according as the pressure number $S \gtrless 1$.

§ 1. Introduction

Recently the subject of the magnetohydrodynamics has become to draw attention of many authors. In particular, the flows of small Reynolds numbers were investigated by Chester,¹⁾ Yosinobu and Kakutani,²⁾ mostly using Stokes approximation. Chester investigated the effect of the longitudinal magnetic field on the flow past a sphere and obtained the drag coefficient as a function of the Hartmann number M alone.

In the present paper the same problem is discussed using Oseen approximation. If we suppose that the deviations of both the flow and magnetic fields from undisturbed ones are very small, and neglect second order terms, the governing equations are linearized. Such a treatment in magnetohydrodynamics has been developed by Yosinobu³⁾ for the analysis of the flow past a circular cylinder. The drag coefficient obtained by him has a singularity at the pressure number $S=1$, namely, it vanishes there abruptly. The dependence of the drag formula on various parameters, particularly on S , is also a very interesting subject in the three-dimensional problem. In the last section we discuss some characters of the flow and the magnetic fields, and the difference between the two- and three-dimensional problems.

§ 2. Fundamental Equations and Oseen Approximation

We investigate the steady flow of an incompressible, viscous, electrically conducting fluid past a sphere in the presence of a uniform magnetic field parallel to the undisturbed flow.

Here we confine ourselves to the fairly slow motion and employ Oseen approximation for calculating the flow and the magnetic fields.

The fundamental equations for this problem are:

(1) Maxwell equations:

$$\text{div } \mathbf{E} = 4\pi c^2 q / \varepsilon, \quad (2.1)$$

$$\text{div } \mathbf{H} = 0, \quad (2.2)$$

$$\text{curl } \mathbf{E} = 0, \quad (2.3)$$

$$\text{curl } \mathbf{H} = 4\pi \mathbf{j}; \quad (2.4)$$

(2) Ohm's law:

$$\mathbf{j} = \sigma(\mathbf{E} + \mu_p \mathbf{U} \times \mathbf{H}); \quad (2.5)$$

(3) The modified Navier-Stokes equation:

$$\rho_a(\mathbf{U} \cdot \text{grad}) \mathbf{U} = -\text{grad } p + \rho_a \nu \nabla^2 \mathbf{U} + \mu_p \mathbf{j} \times \mathbf{H}; \quad (2.6)$$

(4) The equation of continuity:

$$\text{div } \mathbf{U} = 0. \quad (2.7)$$

Here, $\mathbf{E}$ is the electric field, $\mathbf{H}$ the magnetic field, $\mathbf{j}$ the current density, q the excess charge density, ε the dielectric constant, μ_p the magnetic permeability, σ the electrical conductivity, c the speed of light, $\mathbf{U}$ the fluid velocity, p the pressure, ρ_a the fluid density and ν the kinematic coefficient of viscosity of the fluid. All electromagnetic quantities are measured in electromagnetic unit. Both ε and μ_p are assumed to be constant.

In the present problem, we use the cylindrical polar coordinate (r', ϕ', z') , and take the origin at the centre of the sphere, with the z' -axis in the direction of the undisturbed flow. Now we consider an axisymmetric problem in which the ϕ' -derivatives of the velocity and the magnetic intensity, together with their ϕ' -components, all vanish. Then Eq. (2.4) gives $\mathbf{j} = (0, J_\phi, 0)$. On the other hand,

from Eq. (2.5) $\mathbf{E}=(0, E_\phi, 0)$, and together with Eq. (2.3) it follows that $r'\mathbf{E}=\text{constant}=0$ which has been determined by the conditions at infinity upstream: $\mathbf{U}=(0, 0, U)$ and $\mathbf{H}=(0, 0, H)$. Therefore Eq. (2.1) yields $q=0$. Eliminating the current density $\mathbf{j}$, the fundamental equations (2.2) and (2.4)~(2.7) reduce to the following equations in the cylindrical polar coordinate system:

$$(\mathbf{U} \cdot \text{grad}) U_r - \frac{\mu_p}{4\pi\rho_a} (\mathbf{H} \cdot \text{grad}) H_r \\ = -\frac{\partial\tilde{\omega}}{\partial r'} + \nu \left(\nabla^2 U_r - \frac{U_r}{r'^2} \right), \quad (2.8.1)$$

$$(\mathbf{U} \cdot \text{grad}) U_z - \frac{\mu_p}{4\pi\rho_a} (\mathbf{H} \cdot \text{grad}) H_z \\ = -\frac{\partial\tilde{\omega}}{\partial z'} + \nu \nabla^2 U_z, \quad (2.8.2)$$

$$\frac{\partial H_r}{\partial z'} - \frac{\partial H_z}{\partial r'} = 4\pi\sigma\mu_p (U_z H_r - H_z U_r), \quad (2.9)$$

$$\frac{\partial H_r}{\partial r'} + \frac{H_r}{r'} + \frac{\partial H_z}{\partial z'} = 0, \quad (2.2.1)$$

$$\frac{\partial U_r}{\partial r'} + \frac{U_r}{r'} + \frac{\partial U_z}{\partial z'} = 0 \quad (2.7.1)$$

where

$$\left. \begin{aligned} (\mathbf{U} \cdot \text{grad}) &\equiv U_r \frac{\partial}{\partial r'} + U_z \frac{\partial}{\partial z'}, \\ (\mathbf{H} \cdot \text{grad}) &\equiv H_r \frac{\partial}{\partial r'} + H_z \frac{\partial}{\partial z'}, \\ \nabla^2 &\equiv \frac{\partial^2}{\partial r'^2} + \frac{1}{r'} \frac{\partial}{\partial r'} + \frac{\partial^2}{\partial z'^2}, \\ \tilde{\omega} &= \frac{1}{\rho_a} \left(p + \mu_p \frac{H^2}{8\pi} \right). \end{aligned} \right\} \quad (2.10)$$

Now, let the fluid velocity and the magnetic field at any point have components $U+u'_z$, u'_r and $H+h'_z$, h'_r respectively, so that u'_z , u'_r and h'_z , h'_r are the velocity and the magnetic fields due to the disturbances. If, then, we assume that the disturbances are so small that squares and products of them are negligible in the above equations, we have

$$U \frac{\partial u'_r}{\partial z'} - \frac{\mu_p}{4\pi\rho_a} H \frac{\partial h'_r}{\partial z'} \\ = -\frac{\partial\tilde{\omega}}{\partial r'} + \nu \left(\nabla^2 u'_r - \frac{u'_r}{r'^2} \right), \quad (2.11.1)$$

$$U \frac{\partial u'_z}{\partial z'} - \frac{\mu_p}{4\pi\rho_a} H \frac{\partial h'_z}{\partial z'} = -\frac{\partial\tilde{\omega}}{\partial z'} + \nu \nabla^2 u'_z, \quad (2.11.2)$$

$$\frac{\partial h'_r}{\partial z'} - \frac{\partial h'_z}{\partial r'} = 4\pi\sigma\mu_p (U h'_r - H u'_r), \quad (2.12)$$

$$\frac{\partial u'_r}{\partial r'} + \frac{u'_r}{r'} + \frac{\partial u'_z}{\partial z'} = 0, \quad (2.13)$$

$$\frac{\partial h'_r}{\partial r'} + \frac{h'_r}{r'} + \frac{\partial h'_z}{\partial z'} = 0. \quad (2.14)$$

Introducing non-dimensional quantities:

$$u_r = \frac{u'_r}{U}, \quad u_z = \frac{u'_z}{U}, \quad h_r = \frac{h'_r}{H}, \quad h_z = \frac{h'_z}{H} \\ r = \frac{r'}{a}, \quad z = \frac{z'}{a}, \quad \Pi = \frac{\tilde{\omega}}{U^2},$$

these equations become

$$\frac{\partial u_r}{\partial z} - S \frac{\partial h_r}{\partial z} = -\frac{\partial \Pi}{\partial r} + \frac{1}{R} \left(\nabla^2 u_r - \frac{u_r}{r^2} \right) \quad (2.15.1)$$

$$\frac{\partial u_z}{\partial z} - S \frac{\partial h_z}{\partial z} = -\frac{\partial \Pi}{\partial z} + \frac{1}{R} \nabla^2 u_z, \quad (2.15.2)$$

$$\frac{\partial h_r}{\partial z} - \frac{\partial h_z}{\partial r} = R_m (h_r - u_r), \quad (2.16)$$

$$\frac{\partial u_r}{\partial r} + \frac{u_r}{r} + \frac{\partial u_z}{\partial z} = 0, \quad (2.17)$$

$$\frac{\partial h_r}{\partial r} + \frac{h_r}{r} + \frac{\partial h_z}{\partial z} = 0, \quad (2.18)$$

where $R=Ua/\nu$ is the Reynolds number, $R_m=4\pi\sigma Ua\mu_p$ the magnetic Reynolds number, $S=\mu_p H^2/4\pi\rho_a U^2$ the pressure number, a being the radius of the sphere.

It is obvious from Eqs. (2.17) and (2.18) that there exist the stream function ψ and the magnetic stream function χ such that the velocity and the magnetic field components are expressed by

$$u_r = -\frac{1}{r} \frac{\partial \psi}{\partial z}, \quad u_z = \frac{1}{r} \frac{\partial \psi}{\partial r}, \quad (2.19)$$

$$h_r = -\frac{1}{r} \frac{\partial \chi}{\partial z}, \quad h_z = \frac{1}{r} \frac{\partial \chi}{\partial r}. \quad (2.20)$$

Eliminating the pressure term Π from Eqs. (2.15.1) and (2.15.2), we have two basic equations of the problem as follows:

$$\Delta \{ \Delta \psi - R \frac{\partial}{\partial z} (\psi - S\chi) \} = 0, \quad (2.21)$$

$$\Delta \chi - R_m \frac{\partial}{\partial z} (\chi - \psi) = 0, \quad (2.22)$$

where

$$\Delta \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}.$$

The governing equation valid within the sphere is easily obtained. In the sphere $\mathbf{E}=q=\mathbf{j}=0$, and $\text{curl } \mathbf{H}=\text{div } \mathbf{H}=0$. Thus,

$$\Delta \chi = 0. \quad (2.23)$$

§ 3. Boundary Conditions and General Solutions

The boundary conditions for the velocity field are the same as those in ordinary hydrodynamics, namely, at a great distance from the sphere the velocity due to the disturbances vanishes, and the total velocity at the surface of the sphere must vanish. Thus we have

$$u_r = u_z = 0 \quad \text{at infinity,} \quad (3.1)$$

$$\left. \begin{array}{l} u_r = 0 \\ u_z = -1 \end{array} \right\} \text{at the surface of the sphere.} \quad (3.2)$$

On the other hand, the boundary conditions for the magnetic field are that both the tangential component of the magnetic field and the normal component of the magnetic induction are continuous at the surface of the sphere, and the magnetic field due to the disturbances vanishes at infinity. Then we have

$$h_r = h_z = 0 \quad \text{at infinity,} \quad (3.3)$$

$$\left. \begin{array}{l} H_{\theta 0} = H_{\theta i} \\ B_{n0} = B_{ni} \end{array} \right\} \text{at the surface of the sphere,} \quad (3.4)$$

where H and B denote total quantities.

Now eliminating ψ from Eqs. (2.21) and (2.22), we have an equation for determining χ :

$$\Delta \left(\Delta - 2\alpha \frac{\partial}{\partial z} \right) \left(\Delta - 2\beta \frac{\partial}{\partial z} \right) \chi = 0, \quad (3.5)$$

where

$$4\alpha = R + R_m + \sqrt{(R - R_m)^2 + 4M^2},$$

$$4\beta = R + R_m - \sqrt{(R - R_m)^2 + 4M^2},$$

and $M^2 = RR_m S$ is the Hartmann number.

The solution of this equation can be easily obtained in the form:

$$\chi = \chi_1 + \chi_2 + \chi_3, \quad (3.6)$$

where χ_l 's ($l=1, 2, 3$) are the solutions of the following equations respectively:

$$\Delta \chi_1 = 0, \quad \left(\Delta - 2\alpha \frac{\partial}{\partial z} \right) \chi_2 = 0, \quad \left(\Delta - 2\beta \frac{\partial}{\partial z} \right) \chi_3 = 0. \quad (3.7)$$

Then substituting (3.6) and (3.7) into (2.22), we obtain the solution for ψ in terms of χ_l :

$$\psi = \chi_1 + \left(1 - 2 \frac{\alpha}{R_m} \right) \chi_2 + \left(1 - 2 \frac{\beta}{R_m} \right) \chi_3. \quad (3.8)$$

The solution of (2.23) may be written as χ_4 , say, so that

$$\Delta \chi_4 = 0. \quad (3.9)$$

Using the polar coordinate system (ρ, θ, ϕ) , the boundary conditions (3.2) and (3.4) are now expressed in terms of χ ; at $\rho=1$

$$\frac{\partial \chi_1}{\partial \mu} + \left(1 - 2 \frac{\alpha}{R_m} \right) \frac{\partial \chi_2}{\partial \mu} + \left(1 - 2 \frac{\beta}{R_m} \right) \frac{\partial \chi_3}{\partial \mu} = \mu, \quad (3.2.1)$$

$$\frac{\partial \chi_1}{\partial \rho} + \left(1 - 2 \frac{\alpha}{R_m} \right) \frac{\partial \chi_2}{\partial \rho} + \left(1 - 2 \frac{\beta}{R_m} \right) \frac{\partial \chi_3}{\partial \rho} = \mu^2 - 1, \quad (3.2.2)$$

$$\frac{\partial \chi_1}{\partial \rho} + \frac{\partial \chi_2}{\partial \rho} + \frac{\partial \chi_3}{\partial \rho} = \frac{\partial \chi_4}{\partial \rho}, \quad (3.4.1)$$

$$\mu - \frac{\partial \chi_1}{\partial \mu} - \frac{\partial \chi_2}{\partial \mu} - \frac{\partial \chi_3}{\partial \mu} = \kappa \left(\mu - \frac{\partial \chi_4}{\partial \mu} \right), \quad (3.4.2)$$

where $\rho^2 = r^2 + z^2$ and $\mu = \cos \theta$, and $\kappa = \mu_s / \mu_f$ is the ratio of the magnetic permeability of the sphere to that of the fluid.

Taking the boundary conditions at infinity (3.1) and (3.3) into consideration, we have the analytical expressions for χ_l as follows:

$$\chi_1 = (g + g_0 \mu) + \sum_{n=1}^{\infty} g_n \rho^{-n} (1 - \mu^2) P_n'(\mu), \quad (3.10)$$

$$\chi_2 = \sqrt{\frac{2\alpha\rho}{\pi}} e^{\alpha\rho\mu} \left[(A + A_0 \mu) K_{\frac{1}{2}}(\alpha\rho) + \sum_{n=1}^{\infty} A_n K_{n+\frac{1}{2}}(\alpha\rho) (1 - \mu^2) P_n'(\mu) \right], \quad (3.11)$$

$$\chi_3 = \left\{ \begin{array}{l} \sqrt{\frac{2\beta\rho}{\pi}} e^{\beta\rho\mu} \left[(a + a_0 \mu) K_{\frac{1}{2}}(\beta\rho) + \sum_{n=1}^{\infty} a_n K_{n+\frac{1}{2}}(\beta\rho) (1 - \mu^2) P_n'(\mu) \right] \quad \text{for } \beta > 0, \\ \sqrt{\frac{2\beta_0\rho}{\pi}} e^{-\beta_0\rho\mu} \left[(a + a_0 \mu) K_{\frac{1}{2}}(\beta_0\rho) + \sum_{n=1}^{\infty} a_n K_{n+\frac{1}{2}}(\beta_0\rho) (1 - \mu^2) P_n'(\mu) \right] \quad \text{for } \beta < 0, \end{array} \right\} \quad (3.12)$$

$$\chi_4 = \sum_{n=1}^{\infty} G_n \rho^{n+1} (1 - \mu^2) P_n'(\mu), \quad (3.13)$$

where for $\beta > 0$: $A = A_0$, $a = a_0$, $g = g_0$ and

$$g_0 = (2 \frac{\alpha}{R_m} - 1) A_0 + (2 \frac{\beta}{R_m} - 1) a_0,$$

for $\beta < 0$: $\beta_0 = -\beta$, $A = A_0$, $a = -a_0$,

$$g = (1 - 2 \frac{\beta}{R_m}) a_0 - (1 - 2 \frac{\alpha}{R_m}) A_0,$$

$$g_0 = (2 \frac{\alpha}{R_m} - 1) A_0 + (2 \frac{\beta}{R_m} - 1) a_0.$$

Here, $P_n(\mu)$ is the Legendre polynomial of degree n , $K_n(x)$ the modified Bessel function of order n and the primes denote differentiation with respect to μ , and a_n , A_n , g_n and G_n are arbitrary constants.

§ 4. Fulfilment of the Boundary Conditions

We now determine the constants in the general solution by making use of the boundary conditions (3.2.1)~(3.4.2). For this purpose we expand each term in the general solution into spherical harmonics. In this process we must seek for the coefficients of expansion $X_{m,n}$ and $\Psi_{m,n}$ defined as (Goldstein 1929)⁴⁾

$$\left. \begin{aligned} e^{\xi\mu} P_n'(\mu) &= \sum_{m=1}^{\infty} X_{m,n}(\xi) P_m'(\mu), \\ e^{\xi\mu} P_n(\mu) &= \sum_{m=0}^{\infty} \Psi_{m,n}(\xi) P_m(\mu). \end{aligned} \right\} \quad (4.1)$$

They are given by the following recurrence formulae:

$$\left. \begin{aligned} \text{i)} \quad & (n-1)X_{m,n} = (2n-1)X'_{m,n-1} - nX_{m,n-2}, \\ & X_{m,0} = 0, \quad X_{m,1} = \Phi_m/\xi; \\ \text{ii)} \quad & n\Psi_{m,n} = (2n-1)\Psi'_{m,n-1} - (n-1)\Psi_{m,n-2}, \\ & \Psi_{m,0} = \Phi_m, \quad \Psi_{m,1} = \frac{m}{2m-1} \Phi_{m-1} + \frac{m+1}{2m+3} \Phi_{m+1}, \\ \text{iii)} \quad & \Phi_m = (2m+1) \sqrt{\frac{\pi}{2\xi}} I_{m+\frac{1}{2}}(\xi), \end{aligned} \right\} \quad (4.2)$$

where $I_n(\xi)$ is the modified Bessel function of order n .

The various derivatives in Eqs. (3.2.1)~(3.4.2) can be obtained from (3.10)~(3.13). If we substitute them into (3.2.1)~(3.4.2) and expand in series of P_n and P_n' , we obtain an infinite system of simultaneous equations for determining a_n , A_n , g_n and G_n . In these equations, unknown constants g_n and G_n , the coefficients of the harmonic part in the general solution, can be easily eliminated, obtaining finally equations for a_n and A_n .

Hereafter we shall consider the following two cases separately:

Case 1: $\beta > 0$, which corresponds to $S < 1$;

Case 2: $\beta < 0$, which corresponds to $S > 1$.

Case 1. $\beta > 0$.

The equations to be fulfilled by a_n and A_n are

$$\left. \begin{aligned} \alpha A_0 + \beta a_0 &= 0, \\ \sum_{n=0}^{\infty} \{T_{m,n} A_n + t_{m,n} a_n\} &= 3\delta_{m1}, \\ \sum_{n=0}^{\infty} \{S_{m,n} A_n + s_{m,n} a_n\} &= 0 \text{ for } m \geq 1, \end{aligned} \right\} \quad (4.3)$$

where

$$\left. \begin{aligned} T_{m,n}(\alpha) &= (1 - 2 \frac{\alpha}{R_m}) \{ A_{m,n}(\alpha) - (m+1) \Omega_{m,n}(\alpha) \}, \\ S_{m,n}(\alpha) &= \frac{2\alpha}{R_m} \{ A_{m,n}(\alpha) + \kappa m \Omega_{m,n}(\alpha) \}, \end{aligned} \right\} \quad (4.4)$$

$$t_{m,n}(\beta) = T_{m,n}(\beta), \quad s_{m,n}(\beta) = S_{m,n}(\beta), \quad (4.5)$$

and

$$\begin{aligned} \Omega_{m,0}(\alpha) &= -\alpha \sqrt{\frac{2\alpha}{\pi}} K_{\frac{1}{2}}(\alpha) X_{m,1}(\alpha), \\ \Omega_{m,n}(\alpha) &= \alpha \sqrt{\frac{2\alpha}{\pi}} \left[-\frac{n}{2n+1} \{ K_{n+\frac{1}{2}}(\alpha) X_{m,n+1}(\alpha) - K_{n+\frac{3}{2}}(\alpha) X_{m,n}(\alpha) \} \right. \\ &\quad \left. - \frac{n+1}{2n+1} \{ K_{n-\frac{1}{2}}(\alpha) X_{m,n}(\alpha) - K_{n+\frac{1}{2}}(\alpha) X_{m,n-1}(\alpha) \} \right] \\ &\quad \text{for } n \geq 1, \end{aligned} \quad (4.6)$$

$$A_{m,0}(\alpha) = \sqrt{\frac{2\alpha}{\pi}} K_{\frac{1}{2}}(\alpha) [\alpha \{ \Psi_{m,0}(\alpha) + \Psi_{m,1}(\alpha) \} + \Psi_{m,0}(\alpha)],$$

$$A_{m,n}(\alpha) = \sqrt{\frac{2\alpha}{\pi}} K_{n+\frac{1}{2}}(\alpha) \left[\frac{n(n+1)}{2n+1} \alpha \{ \Psi_{m,n-1}(\alpha) - \Psi_{m,n+1}(\alpha) \} - n(n+1) \Psi_{m,n}(\alpha) \right] \text{ for } n \geq 1, \quad (4.7)$$

$$\delta_{m1} = \begin{cases} 1 & \text{for } m=1, \\ 0 & \text{for } m \neq 1. \end{cases}$$

Since it is difficult to solve generally this system of simultaneous equations, we consider a special case in which $\alpha = \beta = O(\delta)$ where δ is a certain small quantity. Thus we obtain

$$\begin{aligned} \alpha A_0 &= \frac{3R_m}{8(\beta - \alpha)} \left[1 + \frac{3}{8} R - \left\{ \frac{19}{320} R^2 + \frac{2M^2}{5(2+\kappa)} \right\} \right. \\ &\quad \left. + \left\{ \frac{1}{7680} (213R^3 + 256RM^2 - 704R_m M^2) + \frac{M^2(R+4R_m)}{10(2+\kappa)} \right\} + O(\delta^4) \right]. \end{aligned} \quad (4.8)$$

Case 2. $\beta < 0$.

The equations for a_n and A_n in this case are mostly analogous to those in Case 1. They are

$$\left. \begin{aligned} \alpha A_0 - \beta_0 a_0 &= 0, \\ \sum_{n=0}^{\infty} \{ T_{m,n} A_n + t_{m,n}^* a_n \} &= 3 \delta_{m1}, \\ \sum_{n=0}^{\infty} \{ S_{m,n} A_n + s_{m,n}^* a_n \} &= 0 \quad \text{for } m \geq 1, \end{aligned} \right\} \quad (4.9)$$

where

$$\left. \begin{aligned} s_{m,n}^*(\beta_0) &= (-1)^{m+n+1} S_{m,n}(\beta_0), \\ t_{m,n}^*(\beta_0) &= (-1)^{n+m} \left(1 + 2 \frac{\beta_0}{R_m} \right) \{ A_{m,n}(\beta_0) - (m+1) \Omega_{m,n}(\beta_0) \}, \end{aligned} \right\} \quad (4.10)$$

Again if we assume that $\alpha = \beta_0 = O(\delta)$, we obtain

$$\begin{aligned} \alpha A_0 &= - \frac{3R_m}{8(\alpha + \beta_0)} \left[1 + \frac{3(R^2 - RR_m + 2M^2)}{8\{(R - R_m)^2 + 4M^2\}^{1/2}} - \frac{19R^2(R + R_m)^2 + (M^2 - RR_m)(76R^2 - 180M^2)}{320\{(R - R_m)^2 + 4M^2\}} \right. \\ &\quad - \frac{2M^2}{5(2+\kappa)} + \frac{1}{7680\{(R - R_m)^2 + 4M^2\}^{3/2}} \left\{ (R + R_m)^3 (213R^3 + 256RM^2 - 704R_m M^2) \right. \\ &\quad \left. + 2(M^2 - RR_m)(639R^4 - 2112R_m^2 M^2 - 1196M^4 - 298M^2 RR_m + 213R^2 R_m^2 + 1470M^2 R^2) \right\} \\ &\quad \left. + \frac{M^2(R^2 + 3RR_m + 4R_m^2 + 2M^2)}{10(2+\kappa)\{(R - R_m)^2 + 4M^2\}^{1/2}} + O(\delta^4) \right] \end{aligned} \quad (4.11)$$

§ 5. Force on the Sphere

The force acting on the sphere is only the drag D along the z -axis and is expressed by

$$D = \int_{S'} \left[\rho_a \nu \left\{ l \left(\frac{\partial U_x}{\partial z'} + \frac{\partial U_z}{\partial x'} \right) + m \left(\frac{\partial U_z}{\partial y'} + \frac{\partial U_y}{\partial z'} \right) + 2n \frac{\partial U_z}{\partial z'} \right\} - np \right. \\ \left. + \frac{\mu_p}{4\pi} (lH_xH_z + mH_yH_z + nH_z^2 - \frac{1}{2}nH^2) - \rho_a U_z U_n \right] dS', \quad (5.1)$$

where S' is an arbitrary closed surface including the sphere. Again neglecting the second order terms of the velocity and the magnetic intensity due to the disturbances, and making use of the stream function and the magnetic stream function, we have the drag coefficient in non-dimensional form as:

$$C_D = \frac{D}{6\pi\nu\rho_a Ua} \\ = \frac{R}{3} \int_{-1}^1 \left(\frac{1}{R} \frac{1}{\rho} \Delta\phi - \mu P - \frac{\mu}{r} \frac{\partial\phi}{\partial r} \right) \rho^2 d\mu, \quad (5.2)$$

where a spherical surface is taken as S' .

The pressure term in this equation is evaluated by integrating (2.15.2) with respect to z :

$$P = -\frac{S}{2} - \frac{1}{r} \frac{\partial}{\partial r} (\chi_1 + S\chi_2 + S\chi_3). \quad (5.3)$$

Putting (5.3), (3.8) and (3.10)~(3.12) into (5.2),

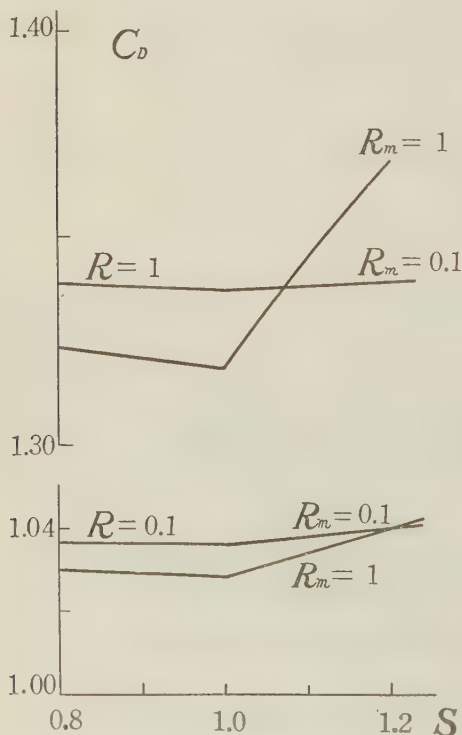


Fig. 1. Drag coefficient C_D in the neighbourhood of $S=1$.

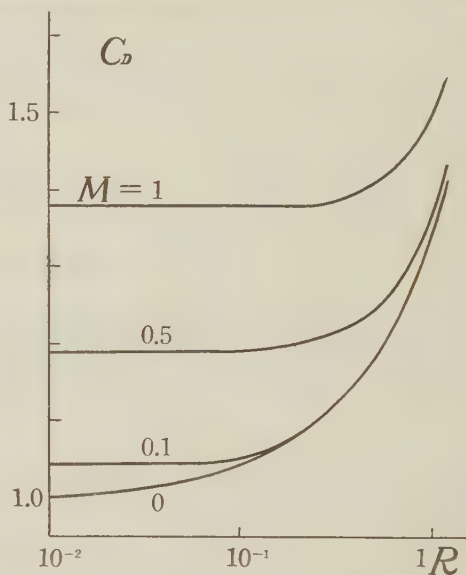


Fig. 2. Drag coefficient C_D versus R . ($R_m=0$, $\kappa=1$).

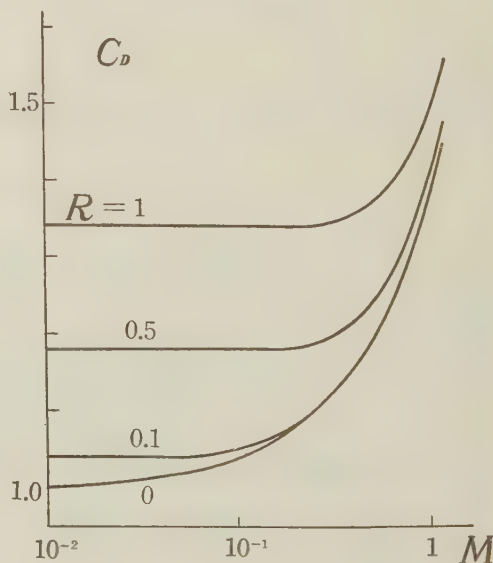


Fig. 3. Drag coefficient C_D versus M . ($R_m=0$, $\kappa=1$).

we get the final formula of the drag coefficient as:

$$C_D = \frac{8}{3R_m} (\beta - \alpha) \alpha A_0 \quad (5.4)$$

for the both cases $S \geq 1$, where αA_0 has already been given by (4.8) and (4.11) for $S < 1$ and $S > 1$ respectively. Making use of these formulae, the values of C_D are calculated for small values of parameters. The results are plotted in Figs. 1, 2 and 3.

§ 6. Discussions

In the preceding sections the velocity and the magnetic fields have been calculated. Then the related quantities such as the vorticity ω and the electric current density $\mathbf{j}$ will be obtained by evaluating $-\frac{1}{r}\Delta\psi$ and $-\frac{1}{r}\Delta\chi$ respectively:

$$\omega_\phi = \frac{2}{r} \left(2 \frac{\alpha}{R_m} - 1 \right) \alpha \frac{\partial \chi_2}{\partial z} + \frac{2}{r} \left(2 \frac{\beta}{R_m} - 1 \right) \beta \frac{\partial \chi_3}{\partial z}, \quad (6.1)$$

$$J_\phi = -\frac{1}{2\pi r} \left\{ \alpha \frac{\partial \chi_2}{\partial z} + \beta \frac{\partial \chi_3}{\partial z} \right\}, \quad (6.2)$$

and these equations show that ω and $\mathbf{j}$ have the similar character to each other. When ρ is large,

$$K_{n+\frac{1}{2}}(\alpha\rho) \approx \sqrt{\frac{\pi}{2\alpha\rho}} e^{-\alpha\rho},$$

so that it is seen from (3.11) that the χ_2 -terms behave like $\exp \alpha\rho(\mu-1)$ for large ρ . Then the terms in ω and $\mathbf{j}$ which depend on χ_2 are proportional to $\exp(-2\alpha\rho \sin^2 \frac{\theta}{2})$, and there-

fore they become vanishingly small for large ρ except for the region in which $\theta < k\rho^{-\frac{1}{2}}$ where k is a small constant. This region which extends downstream of the sphere in the shape of paraboloid is usually referred to as the wake. Thus, the χ_2 -terms are found to give rise to the distribution, of the vorticity and the electric current density, which corresponds to the wake in ordinary hydrodynamics. Similarly, for large ρ the χ_3 -terms behave like $\exp(-2\beta\rho \sin^2 \frac{\theta}{2})$ for $\beta > 0$ and $\exp(2\beta\rho \cos^2 \frac{\theta}{2})$ for $\beta < 0$ respectively. Therefore, it gives also the wake-like structure for the vorticity and electric current density. In this case, however, the wake appears downstream ($\theta < k\rho^{-\frac{1}{2}}$) for $\beta > 0$ (i.e. $S < 1$), and upstream ($\pi - \theta < k\rho^{-\frac{1}{2}}$) for $\beta < 0$ (i.e. $S > 1$). This behaviour of the wake is quite similar to that in the two-dimensional case treated by Yosinobu,

Since the drag coefficient C_D has different expressions according as $S \geq 1$, it has a singularity at $S=1$ as shown graphically in Fig. 1. The curves of C_D are continuous but not analytical at $S=1$ and have different right- and left-differential coefficients there, while in the two-dimensional problem a singularity of the type $1/\log|S-1|$ is found at $S=1$.

It may be of interest to consider why the behaviour of the drag coefficient in the neighbourhood of $S=1$ differs for two- and three-dimensional cases. In the present case the equation for the vorticity is written as

$$\left(\Delta - 2\alpha \frac{\partial}{\partial z} \right) \left(\Delta - 2\beta \frac{\partial}{\partial z} \right) (r\omega_\phi) = 0. \quad (6.3)$$

For $S=1$ (i.e. $\beta=0$), this equation reduces to

$$\left(\Delta - 2\alpha \frac{\partial}{\partial z} \right) \Delta (r\omega_\phi) = 0, \quad (6.4)$$

the solution of which is given as a linear combination of the solutions of equations:

$$\left(\Delta - 2\alpha \frac{\partial}{\partial z} \right) (r\omega_\phi) = 0 \text{ and } \Delta (r\omega_\phi) = 0. \quad (6.5)$$

The equation $\Delta(r\omega_\phi)=0$ is nothing but the fundamental equation for the steady flow in ordinary hydrodynamics for extremely low Reynolds numbers (Stokes approximation). The two- and the three-dimensional flow problems with a circular cylinder and a sphere as the solid boundaries respectively were already solved using Stokes approximation, and it is well known that there is no solution for the former problem whereas a solution exists for the latter. The same is true for the solutions of Eq. (6.3), since the solution of the first equation of (6.5) is shown not to contribute to the boundary condition at infinity. Thus, the fact that we have obtained the vanishing drag coefficient and a finite one at $S=1$ for the two- and the three-dimensional problems respectively may be explained as the reflexion of the above circumstances.

In various limiting cases, the formula (5.4) for the drag coefficient agrees with the results already obtained by Chester, Goldstein and Stokes. Thus, if $R=R_m=0$ but $M \neq 0$ and $\kappa=1$ (in this case $S=\infty$), (5.4) together with (4.11) gives Chester's result:

$$C_D = 1 + \frac{3}{8}M + \frac{7}{960}M^2 - \frac{43}{7680}M^3 + O(M^4).$$

Also, if $M=0$ and $R \neq 0$ (so that $R_m=0$ or

$S=0$), (5.4) together with (4.8) reduces to Goldstein's result:

$$C_D=1+\frac{3}{8}R-\frac{19}{320}R^2+\frac{71}{2560}R^3+O(R^4).$$

Further, putting $R=R_m=M=0$, we get Stokes formula: $C_D=1$.

For $S=1$, the expressions of the drag coefficient for both cases ($S\geq 1$) agree with each other, giving

$$\begin{aligned} C_D=1+\frac{3}{8}R-\left\{\frac{19}{320}R^2+\frac{2RR_m}{5(2+\kappa)}\right\} \\ +\left\{\frac{1}{7680}(213R^3+256R^2R_m-704RR_m^2) \right. \\ \left. +\frac{RR_m(R+4R_m)}{10(2+\kappa)}\right\}+O(\delta^4). \end{aligned}$$

It should be noted that the effect of the ratio of the permeabilities, κ , appears first in the second order terms in the drag coefficient, and that C_D has always a minimum at $S=1$.

In the above analysis, we have dealt with the uniform flow past a sphere at rest. However, the problem in which a sphere moves with a uniform velocity through a fluid at rest can be discussed in the same way, and we

have the analogous result except for the electric field E . When E is transformed from the present system to the moving one, it has the component $\mu_p \boldsymbol{U} \times \boldsymbol{H}$ where $\boldsymbol{U}$ is the velocity of the sphere and $\boldsymbol{H}$ is the magnetic field given in the present case. There is no more difference between the cases where magnetic field is fixed to the fluid and to the obstacle respectively.

Acknowledgements

The writer wishes to express his cordial thanks to Professor S. Tomotika for his encouragement throughout this study, and his kind inspection of the manuscript. His thanks are also due to Messrs. Yosinobu and Kakutani for their helpful advices and discussions.

References

1) W. Chester: J. Fluid Mech. **3** (1957) 304.
2) H. Yosinobu and T. Kakutani: J. Phys. Soc. Japan **14** (1959) 1433.
3) H. Yosinobu: J. Phys. Soc. Japan **15** (1960)
4) S. Goldstein: Proc. Roy. Soc. A, **123** (1929) 225.

Errata

Relative Intensities of Zeeman Components in Nuclear Quadrupole Resonance Spectrum

By Masaharu TOYAMA

J. Phys. Soc. Japan **14** (1959) 1727

Page	Column	Line		Should be read
1728	right	7 from the bottom	states	state
		3 from the bottom	and $\pm m' M \rightleftharpoons \pm m'' M$,	and $\pm m' M \rightleftharpoons \mp m'' M$,
1729	left	1	$\mathcal{H}^\circ$	$\mathcal{H}_\circ$
1732		3 in Eq. (21)	$\frac{\eta_-}{3}$	$\frac{\eta}{3}$
1733		2 in Eq. (33)	$I_{y,3/2,3/2}=-\frac{1}{2\rho}\cdots$	$I_{y,3/2,3/2}=\frac{1}{2\rho}\cdots$
		the last of Eq. (25)	$\frac{3\eta_-}{4\rho^4}$	$\frac{\eta^2}{4\rho^4}$
1736	left	30	Li	Li ⁶
1737		4 in Eq. (29)	$+\eta^2(H_x^2-H_y^2)$	$+\eta^2(H_x^2+H_y^2)$
		9 in Eq. (29)	$\frac{1}{216}$	$\frac{1}{432}$

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm×7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 197

Effect of Charged Dislocation on the Thermoelectric Power of Semiconductors*

By Tokio OHTA

Department of Physics, Defense Academy,
Yokosuka

(Received November 24, 1959)

It has been accepted that edge dislocations in N-Ge act as rows of closely spaced acceptor-centers and a dislocation accepts electrons to become a line of negative charge surrounded by the cylindrical layer of positive space charge. Read¹⁾ has studied the effects of the cylinder of the space charge on the electrical conductivity and Hall mobility of semiconductors. Here we report the effects of the cylinder on the thermoelectric power (T.E.P.) in semiconductors. We assume the random distribution of the sectional centers of the cylinders of which directions of length are parallel to each other. The used notations are as follows. Q : T.E.P., N_b : density of impurities which reserve electrons at 0°K, N_a : density of dislocations, N_1 : density of donor impurities, N_c : density of chemical acceptors, S : spacing between dangling bonds, $f(T)$: occupation ratio of electron at dislocation acceptors at $T^\circ\text{K}$, δ' : depth of dislocation acceptor level measured from the top of space charge mountain, δ : depth of donor level measured from the bottom of c -band, $-\zeta$: Fermi energy, Δ : energy gap between c - and v -band, x : ratio of electronic mobility by impurity scattering to that by both the cylinder and phonon scattering, K : ratio of electron to hole conductivity, and the others are as usual.

In the impurity range of temperature, the electronic mean free path is comparable to the radius of the cylinder, so that the additivity of the reciprocal mean free paths is held. Neglecting the hole population, we obtain

$$Q = (k/e) [\zeta/kT + \{2 - x^2 + x^3\psi(x)\} / \{1 - x^2\psi(x)\}],$$

where

$$\begin{aligned} \zeta/kT &= \ln [(N_b' - N_1)/2A_e] \\ &+ \{[(N_b' - N_1)/2A_e]^2 + N_1 \exp(-\delta/kT)/A_e\}^{1/2}, \\ N_b' &= N_b - N_a f(0)/S, \\ A_{e,h} &= (1 \mp \epsilon) 2(2\pi m_{e,h} kT)^{3/2} / h^3, \\ \epsilon &= N_a f(T) / S(N_1 - N_c), \end{aligned}$$

$$\varphi(x) = C_i(x) \sin x - S_i(x) \cos x + \frac{1}{2}\pi \cos x,$$

$$\psi(x) = -C_i(x) \cos x - S_i(x) \sin x + \frac{1}{2}\pi \sin x.$$

An appreciable effect is introduced in ζ , however, the contribution from phonon drag to the T.E.P. is so large that the present effect will not be observed separately.

In the transition range of temperature, holes are created not only in the dislocation acceptor level but also in the v -band and the cylinder becomes P-type bulk. The radius of the cylinder decreases but the electronic mean free path becomes far less than it, so that the conducting electron follows curved path that wind around the cylinders. Such distortion of the electronic stream line reduces the apparent mobility. The ratio of apparent to free mobility is denoted by $g(\epsilon)^{1)}$. Then the combined T.E.P. between the mother bulk (Q_0) and the cylinder bulk (Q_c) is given by (Q_c has the usual expression for P-type materials.)

$$Q = \{(1-\epsilon)(1+K)Q_0 + \epsilon Q_c\} / \{1 + (1-\epsilon)K\},$$

where

$$\begin{aligned} Q_0 &= (k/e) \{ -2(Krg(\epsilon) - 1) / (Krg(\epsilon) + 1) + \zeta/kT \\ &+ (\Delta/kT) / (Krg(\epsilon) + 1) \}, \\ \zeta/kT &= \ln [N_b''/2A_e] \\ &+ \{ (N_b''/2A_e)^2 + A_h \exp(-\Delta/kT)/A_e \\ &+ N_a f(0) \exp(-\delta'/kT)/A_c S \}^{1/2}, \end{aligned}$$

$$N_b'' = N_b' - N_a f(0)/S, \quad r = (1-\epsilon)/(1+\epsilon).$$

In this range of temperature, the present effects are prominent especially in the materials for which $N_1 - N_c$ is small, N_a is large, and δ' is near the top of the v -band so that ϵ approaches unity and K becomes small. N-type materials will change their properties to P-type. However, in the common materials such as Ge, the effects will be small, e.g., for the specimen used by Pearson *et al.*²⁾ in which $N_a \approx 3 \times 10^6 \text{ cm}^{-2}$, we estimate $\epsilon = 0.15$, $Krg(\epsilon) = 12.6$ at 340°K and $\epsilon = 0.04$, $Krg(\epsilon) = 1.50$ at 380°K. These values are insufficient to cause appreciable effects.

The author express his cordial thanks to Prof. Y. Uemura for his valuable discussions.

References

- 1) W. T. Read: Phil. Mag. **45** (1954) 775, 1119; **46** (1955) 111.
- 2) G. L. Pearson, W. T. Read and F. J. Morin: Phys. Rev. **93** (1954) 666.

* Copies of the full report are available by request.

J. PHYS. SOC. JAPAN **15** (1960) 198

Influence of Foreign Magnetic Nuclei on NMR

By Akira MIYAKE and Riichirô CHÛJÔ

Department of Physics, Faculty of Liberal
Arts and Science, Shizuoka University,
Shizuoka

(Received September 29, 1959)

The theory of NMR in the system involving non-resonating foreign magnetic nuclei has been extended¹⁾ along the general formulation proposed by Kubo and Tomita²⁾. To the isotropic second moment of absorption line in the frequency scale contribute the magnetic interaction between the resonating nuclei:

$$\sigma_0'^2 = \frac{3}{5} \hbar^2 \gamma_0^4 I_0(I_0+1) b_{00}^{-6},$$

$$\sigma_0''^2 = \frac{7}{5} \hbar^2 \gamma_0^4 I_0(I_0+1) b_{00}^{-6}, \quad (1)$$

and one between the resonating and the foreign nuclei:

$$\sigma_f'^2 = \frac{4}{15} \hbar^2 \gamma_0^2 \gamma_f^2 I_f(I_f+1) b_{0f}^{-6},$$

$$\sigma_f''^2 = \frac{16}{15} \hbar^2 \gamma_0^2 \gamma_f^2 I_f(I_f+1) b_{0f}^{-6}, \quad (2)$$

where γ is the gyromagnetic ratio, I the spin quantum number, subscripts 0 and f are concerned with the resonating nuclear species and the foreign species, single prime means the secular contribution which appears in the central line, double prime means the non-secular one which appears in the satellite lines unless the absorption

line is very narrowed,

$$b_{00}^{-6} = \frac{1}{N_0} \sum_{j \in 0} \sum_{k \in 0} \langle r_{jk}^{-6} \rangle_{av},$$

$$b_{0f}^{-6} = \frac{1}{N_0} \sum_{j \in 0} \sum_{k \in 0} \langle r_{jk}^{-6} \rangle_{av}, \quad (3)$$

where r_{jk} is the distance between the j th and the k th nucleus, the summation $j \in 0$ means to be taken over all j belonging to o -species, and so forth.

Eqs. (1) and (2) are the extension of those given by Waller³⁾ and Van Vleck.⁴⁾ Examples of the magnitude of second moment are given for the plane zig-zag configuration chains in Table I.⁵⁾

Table I. Calculated second moments (in gauss²) for H-resonance of polyvinyl-chloride (PVC) and -fluoride (PVF), isotactic (I) and syndiotactic (S).

		$\sigma_0'^2$	$\sigma_0''^2$	$\sigma_f'^2$	$\sigma_f''^2$
PVC	I	13.47	31.43	0.06	0.24
	S	12.81	29.89	0.08	0.32
PVF	I	13.47	31.43	1.24	4.96
	S	12.81	29.89	1.51	6.04

Unless the line width is very narrowed by the thermal motion, using $\sigma^2 = \sigma_0'^2 + \sum_f \sigma_f'^2$ as the second moment, we can take account of the influence of foreign magnetic nuclei on the line contour or the line width $1/T_2$, because the non-secular contribution to the central line is negligible.

In the very narrowed case, however, the non-secular part contributes to the line width additionally by

$$1/T_1' = \frac{1}{5} \hbar^2 \gamma_0^4 I_0(I_0+1) b_{00}^{-6} \left(\frac{5\tau}{1+\omega_0^2\tau^2} + \frac{2\tau}{1+4\omega_0^2\tau^2} \right)$$

$$+ \frac{1}{15} \hbar^2 \gamma_0^2 \sum_f \gamma_f^2 I_f(I_f+1) b_{0f}^{-6} \left\{ \frac{3\tau}{1+\omega_0^2\tau^2} + \frac{6\tau}{1+\omega_f^2\tau^2} + \frac{\tau}{1+(\omega_0-\omega_f)^2\tau^2} + \frac{6\tau}{1+(\omega_0+\omega_f)^2\tau^2} \right\}, \quad (4)$$

and to the spin-lattice relaxation time T_1 by

$$1/T_1 = \frac{1}{5} \hbar^2 \gamma_0^4 I_0(I_0+1) b_{00}^{-6} \left(\frac{2\tau}{1+\omega_0^2\tau^2} + \frac{8\tau}{1+4\omega_0^2\tau^2} \right) + \frac{1}{15} \hbar^2 \gamma_0^2 \sum_f \gamma_f^2 I_f(I_f+1) b_{0f}^{-6} \left\{ \frac{3\tau}{1+\omega_0^2\tau^2} \right.$$

$$\left. + \frac{\omega_f^2}{\omega_0^2} \frac{3\tau}{1+\omega_f^2\tau^2} + \frac{(\omega_0-\omega_f)^2}{\omega_0^2} \frac{\tau}{1+(\omega_0-\omega_f)^2\tau^2} + \frac{(\omega_0+\omega_f)^2}{\omega_0^2} \frac{6\tau}{1+(\omega_0+\omega_f)^2\tau^2} \right\}, \quad (5)$$

where ω_0 and ω_f are respective resonance angular frequencies of species o and f , τ is the correlation time of the thermal motion.

References

- 1) A. Miyake and R. Chûjô: Busseiron-Kenkyu Ser. II **2** (1957) 769; Repts. Progr. Polymer Phys. Japan **1** (1958) 171.
- 2) R. Kubo and K. Tomita: J. Phys. Soc. Japan **9** (1954) 888.
- 3) I. Waller: Z. Phys. **79** (1932) 370.
- 4) J. H. Van Vleck: Phys. Rev. **74** (1948) 1168.
- 5) A. Miyake: Busseiron-Kenkyu Ser. II **5** (1959) 334.

J. PHYS. SOC. JAPAN **15** (1960) 199~200**Thermal Conductivity of KNO_3**

By Ikushi YOSHIDA

*Institute for Solid State Physics,
University of Tokyo, Tokyo*

and Shozo SAWADA

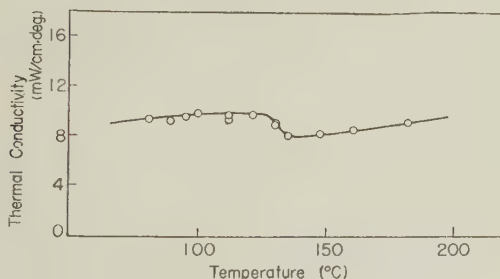
*Tokyo Institute of Technology,
Tokyo*

(Received November 4, 1959)

Potassium nitrate KNO_3 has the aragonite structure D_{2h}^{16} at room temperature (phase II) and is reported to have the calcite structure D_{3d}^6 above 128°C (phase I)¹⁾. A number of interesting investigations have been made concerning the phase transition of this substance^{2),3),4)}, and the phase III which appears between the phases I and II only on cooling has recently been found to be ferroelectric⁵⁾.

We have measured the temperature dependence of the thermal conductivity of KNO_3 and found a distinct anomaly at the transition.

The measurement was made using a comparative method⁶⁾, and specimens were cut out from polycrystals obtained by slow cooling of the melt of potassium nitrate of special pure grade. Fig. 1

Fig. 1. Thermal conductivity of KNO_3 .

shows the temperature dependence from room temperature up to above the transition point. A step-wise decrease at about 130°C is conspicuous. By this method of measurement we were obliged to allow a somewhat large temperature gradient in the specimen, and so the obtained values were only means in about ten degrees temperature range. Taking this into account we suppose that the decrease of thermal conductivity takes place nearly discontinuously. The quantity of the anomaly amounts to more than 20% of the absolute value.

Eucken and Schroeder found a temperature dependence of thermal conductivity which resembles to this in solid hydrogen bromide near the phase transition at 89°K ⁷⁾. As for the cause of such a sudden decrease of the thermal conductivity at transition temperature, we would like to point out at least two possibilities. Thermal expansion coef-

ficient in the phase I is, according to Cohen and Bredée, nearly 20% larger than that in the phase II. Even this fact alone appears, if we accept a theory of Dugdale and McDonald which insists that the mean free path of phonons is inversely proportional to the thermal expansion coefficient⁸⁾, sufficient to explain the above-mentioned sudden decrease of the thermal conductivity. The model they adopted seems, however, very simple and there can perhaps be other mechanisms which influence the thermal conductivity in real complex crystals. The low temperature structure of KNO_3 is analogous to NiAs arrangement and consists of K^+ ions separated by double layers of NO_3^- ions. The latter are arranged antipolar along the b -axis and cannot make a whole rotation about any axis. Above the transition temperature, on the other hand, the double layers of NO_3^- coalesce into a single one, and this change is favourable for the rotation of NO_3^- groups. Indeed, Tahvonen's X-ray investigation⁹⁾ leads to the conclusion that in this form the nitrate groups are rotating about the trigonal axis and the rotation is connected with oscillations in the direction of this axis. The excitation of rotational motions has a good deal of possibilities to couple with phonon waves and to scatter them considerably. A phase transition of sodium nitrite at 160°C is said to be caused not by a serious rearrangement of ions but by an order-disorder transformation of the arrangement of NO_2^- groups. At this phase transition a decrease of thermal conductivity is observed fairly markedly¹⁰⁾. Perhaps there would be a strong resemblance between mechanisms of the decrease of thermal conductivity at phase transitions of KNO_3 and NaNO_2 .

The fact that a small anomaly was found at the phase transition of BaTiO_3 at 120°C where ferroelectricity disappears⁹⁾ rouses interest about the behaviour of temperature dependence of thermal conductivity in the phase III of KNO_3 which is ferroelectric. But nearly the same temperature dependence of thermal conductivity was seen on both heating and cooling. It is possible, however, that any small anomaly might have been obscured by the narrowness of the range of the phase III which is comparable with the above-mentioned temperature gradient necessary for the measurement of thermal conductivity.

Eucken and Kuhn measured the thermal conductivity of KNO_3 at 0°C and -190°C and found a slightly positive temperature dependence¹¹⁾ which was affirmed by our measurement made by the direct method. Low temperature data were continuable to those determined by the comparative method at room temperature, though they were considerably low values compared to those obtained by Eucken and Kuhn.

References

- 1) D. A. Edwards: *Z. Krist.* **80** (1931) 154.
- 2) E. Cohen and H. L. Bredée: *Z. phys. Chem. A*, **140** (1929) 391.
- 3) F. C. Kracek: *J. Phys. Chem.* **34** (1930) 225.
- 4) S. W. Kennedy, A. R. Ubbelohde and I. Woodward: *Proc. Roy. Soc. A*, **219** (1953) 303.
- 5) S. Sawada, S. Nomura and S. Fujii: *J. Phys. Soc. Japan* **13** (1958) 1549.
- 6) I. Yoshida, S. Nomura and S. Sawada: *J. Phys. Soc. Japan* **13** (1958) 1550.
- 7) A. Eucken and E. Schroeder: *Ann. Physik* **36** (1939) 609.
- 8) J. S. Dugdale and D. K. C. MacDonald: *Phys. Rev.* **98** (1955) 1751.
- 9) P. E. Tahvonen: *Ann. Acad. Sci. Fenn. Ser. A*, **1** (1947) 42.
- 10) I. Yoshida and S. Sawada: unpublished.
- 11) A. Eucken and G. Kuhn: *Z. phys. Chem.* **134** (1928) 193.

J. PHYS. SOC. JAPAN **15** (1960) 200

On a Solution of the Paraxial Ray Equation in an Axially Symmetrical Electrostatic Field

By Noboru SHIBATA

*Faculty of Liberal Arts and Education,
Nagasaki University*

(Received September 15, 1959)

In the investigation of the electron optical properties of the so-called Ehrenberg-Spear type X-ray tube,¹⁾ Spear²⁾ has used a method which is a combination of paraxial ray tracing and dynamical determination of the electron trajectory in cathode region. In his method paraxial ray tracing consists of obtaining solutions of the paraxial ray equations of fundamental rays by numerical method, and transforming initial states of motion of any electrons at the beginning of the paraxial region to final ones with the aid of a linear combination of these solutions. However, in an axially symmetrical electrostatic field, the electrostatic potential V at any point is expressed as

$$V(x, y) = \sum_{n=0}^{\infty} (-1)^n \frac{\phi^{(2n)}}{(n!)^2} \left(\frac{y}{2}\right)^{2n}, \quad (1)$$

where x is the distance measured along the symmetry axis, y is the distance from the symmetry axis and ϕ is the axial potential. If the axial potential has a following form

$$\phi(x) = ax^2 + bx + c, \quad (2)$$

where a , b and c are constants, the general ray equation³⁾

$$2V \frac{d^2 y}{dx^2} = \left[\frac{\partial V}{\partial y} - \frac{\partial V}{\partial x} \frac{dy}{dx} \right] \left[1 + \left(\frac{dy}{dx} \right)^2 \right], \quad (3)$$

becomes

$$\frac{d^2 y}{dx^2} + \frac{2ax + b}{2\phi} \frac{dy}{dx} + \frac{a}{2\phi} y = 0, \quad (4)$$

by neglecting the terms $(dy/dx)^2$ and $(1/2)ax^2$ in V (paraxial approximation). By substitution

$$z = \frac{1}{\sqrt{a}} \log \left(\sqrt{ax^2 + bx + c} + x\sqrt{a} + \frac{b}{2\sqrt{a}} \right) \quad \text{for } a > 0, \quad (5)$$

or

$$z = \frac{-1}{\sqrt{-a}} \sin^{-1} \frac{2ax + b}{\sqrt{b^2 - 4ac}} \quad \text{for } a < 0, \quad (5')$$

Eq. (4) reduces to

$$\frac{d^2 y}{dz^2} + \frac{a}{2} y = 0, \quad (6)$$

Thus, we can get an analytical solution of the paraxial ray equation. Therefore, we are led to a following trajectory tracing method in the paraxial region. That is, first, we divide the symmetry axis into several regions such that in each region the measured axial potential could be approximated to a quadratic form in terms of x , within the accuracy to which ϕ is measured, then, in any region we solve Eq. (6) adopting the final state of motion in the prior region for the initial conditions. Repeating these procedures successively, we can get the whole trajectory of any electron in the paraxial region.

This method was applied to the investigation of the electron optical properties of the modified Ehrenberg-Spear type X-ray tube.⁴⁾ It was shown that the error introduced by the approximations mentioned above may not be so serious if the motion of electron is subject to the paraxial conditions, and that the accuracy of this method mainly depends on the exactness of the measured values of the axial potential, especially those in cathode region which strongly affect the behavior of electron.

References

- 1) W. Ehrenberg and W. E. Spear: *Proc. Phys. Soc. London* **64** (1951) 67.
- 2) W. E. Spear: *Proc. Phys. Soc. London* **64** (1951) 233.
- 3) W. W. Harman: *Fundamentals of Electronic Motion* (McGraw-Hill, 1953) 52.
- 4) N. Shibata and S. Tamagusuku: *Sci. Bull. Fac. Liberal Arts and Education, Nagasaki Univ.* **6** (1957) 5.

J. PHYS. SOC. JAPAN **15** (1960) 201**NMR Second Moment of a Radical Oscillating in a Periodic Potential**

By Riichirô CHÛJÔ

*Department of Physics, Shizuoka University,
Shizuoka*

(Received November 9, 1959)

The authors¹⁾ developed the theory of influence of the motion of a radical in a periodic potential upon the second moment of NMR at both high and low temperatures. Although classical statistical mechanics were applied there to both cases, quantum statistico-mechanical treatment is inevitable for the low temperature case. So, in the second moment

$$\Delta H_2^2 = \frac{3}{4} \hbar^2 \gamma^2 I(I+1) \frac{1}{N} \sum_j \sum_k r_{jk}^{-6} g_n(T), \quad (1)$$

the factor

$$g_n(T) = \left\langle \left[\int_{-\pi/n}^{\pi/n} (3 \cos^2 \theta_{jk} - 1) \exp \{ -V_n(\phi)/kT \} d\phi \right. \right. \\ \left. \left. / \int_{-\pi/n}^{\pi/n} \exp \{ -V_n(\phi)/kT \} d\phi \right]^2 \right\rangle_{\text{isotropic mean}} \quad (2)$$

ought to be replaced by

$$g_n(T) = \langle [\text{trace} \{ (3 \cos^2 \theta_{jk} - 1) \exp \{ -\mathcal{H}/kT \} \} / \text{trace} \{ \exp \{ -\mathcal{H}/kT \} \}]^2 \rangle_{\text{isotropic mean}}, \quad (2')$$

where $\mathcal{H}$ is the Hamiltonian for the axial motion of a radical, i.e.

$$\mathcal{H} = -\frac{\hbar^2}{2J} \frac{\partial^2}{\partial \phi^2} + \frac{u}{2} (1 - \cos n\phi),$$

J is the moment of inertia of the radical, and all other notations are identical with those in reference 1).

At low temperatures the motion is almost confined to the bottom of a potential through, so the harmonic oscillator approximation

$$\mathcal{H} \simeq -\frac{\hbar^2}{2J} \frac{\partial^2}{\partial \phi^2} + \frac{n^2 u}{4} \phi^2 \quad (3')$$

may be permitted. Then, Eq. (2') can be calculated²⁾ as

$$g_n(T) \simeq \frac{4}{5} - \frac{6\sqrt{2}}{5n} \left(\frac{\hbar^2}{Ju} \right)^{1/2} \coth \left(\frac{n}{2\sqrt{2}} \sqrt{\frac{u}{JkT}} \right) + \dots \quad (4)$$

In the classical limit ($\hbar \rightarrow 0$), this expression tends to

$$g_n(T) \simeq \frac{4}{5} - \frac{12}{5} (2kT/u) + \dots, \quad (5)$$

which agrees with the classical formula, Eq. (6') in reference 1), except for the higher order terms owing to the adopted approximation, Eq. (3'). But, in the low temperature limit Eq. (4) gives

$$g_n(0) \simeq \frac{4}{5} - \frac{6\sqrt{2}}{5n} \left(\frac{\hbar^2}{Ju} \right)^{1/2} + \dots, \quad (6)$$

which is different from the classical value 4/5 by the terms

$$- \frac{6\sqrt{2}}{5n} \left(\frac{\hbar^2}{Ju} \right)^{1/2} + \dots,$$

which correspond to the reduction of the second moment due to the zero point vibration. In spite of these circumstances, we can verify that

$$\frac{5}{4} g_n(T) \simeq 1 - \frac{12}{n^2} \frac{\langle V_n \rangle}{u} \quad (7)$$

(cf. Eq. (7) in reference 1)) is valid also for quantum mechanical case, where $\langle V_n \rangle$ means

$$\langle V_n \rangle = \frac{\text{trace} \left\{ \frac{u}{2} (1 - \cos n\phi) \exp \{ -\mathcal{H}/kT \} \right\}}{\text{trace} \{ \exp \{ -\mathcal{H}/kT \} \}} \\ \simeq \frac{1}{2} kT + \dots \quad (\text{classical limit}) \\ \simeq \frac{\sqrt{2}}{8} n \left(\frac{\hbar^2 u}{J} \right)^{1/2} + \dots \quad (\text{low temperature limit})$$

The author wishes to express his sincere thanks to Professor K. Tomita (Kyoto University) and Professor A. Miyake (Shizuoka University) for their discussions.

References

- 1) A. Miyake and R. Chûjô: J. Phys. Soc. Japan **14** (1959) 978.
- 2) K. Husimi: Proc. Phys.-Math. Soc. Japan **22** (1940) 264.

J. PHYS. SOC. JAPAN **15** (1960) 201~202**Temperature Dependence of T_1 of Cl^{35} in Para-dichlorobenzene**

By Akira HIRAI

*Department of Physics, Faculty of Science,
Kyoto University, Kyoto*

(Received November 11, 1959)

In pure quadrupole resonance (P.Q.R.), the quadrupolar relaxation plays a most important role in relaxation mechanisms¹⁾. As early as in 1951, Bayer proposed a simple theory on the temperature dependence of the resonance frequency (ν) and the spin-lattice relaxation time (T_1) in P.Q.R.²⁾. The temperature dependence of ν has been measured by many workers³⁾, and for many substances, their data are almost satisfactorily explained by Bayer's theory.

We have measured T_1 of Cl^{35} in para-dichlorobenzene at several temperatures, using 90°-90° pulse method. The apparatus is the same as that we have used for pulsed N.M.R. researches⁴⁾, except that the straight nuclear signal receiver has

been replaced by a superheterodyne system to be suitable to follow the change of ν . The sample has been immersed in an appropriate refrigerant. The obtained data are tabulated below.

Table I. T_1 of Cl^{35} in para-dichlorobenzene.

$T(^{\circ}\text{K})$	$T_1(\text{m sec})$
77	560 ± 50
90	450 ± 40
195	60 ± 5
271	27 ± 3
292	22 ± 2
300	19 ± 2

According to Bayer's theory, T_1 is given, to a certain approximation acceptable in our temperature region, by

$$T_1 \approx T_{11\Delta m_1=2} \approx \frac{16}{3} \cdot \frac{1}{(h\nu_Q)^2} \cdot \frac{(\pi\Theta\nu_t)^2}{\tau_a} \cdot \frac{(\epsilon^x - 1)^2}{4 \cosh x - 3},$$

$$x = \frac{h\nu_t}{kT},$$

where ν_Q is the quadrupole resonance frequency at 0°K , ν_t the frequency of the torsional vibration of molecule, to which the energy of spin system relaxes, Θ the moment of inertia of molecule corresponding to ν_t , τ_a the average life-time in excited states of torsional vibration, which is to be chosen so as to make the experimental data fit to the theoretical one and is assumed to be independent of the temperature.

Now we take the following values: $\nu_Q = 34.8 \times 10^6$ c/sec, as extrapolated from our data on the temperature dependence of ν , $\nu_t = 27 \text{ cm}^{-1} = 81 \times 10^{10}$ c/sec, which is the most effective in quadrupolar relaxation, out of the three torsional vibrational frequencies, 27 cm^{-1} , 54 cm^{-1} , 93 cm^{-1} , obtained by Saksena from Raman spectrum⁵⁾, $\Theta = 1.41 \times 10^{-37}$ gr-cm², as calculated from the molecular structure,

and $\tau_a = 10/\nu_t = 1.23 \times 10^{-11}$ sec, in which the author estimated that each molecule oscillates ten times in any excited state before it makes a transition to the ground state. The theoretical curve thus obtained and the experimental points are shown in the annexed figure. From this figure, we can see that the simple theory by Bayer explains the general feature of data, but more precisely, the experimental curve has a steeper temperature dependence than the theoretical.

To explain this discrepancy by modification of Bayer's theory, we have re-examined Bayer's assumptions and tried to modify his theory and also to include effects of other vibration modes and of the volume change. But, so far we could not find any good explanation for this discrepancy by simple modification of Bayer's theory. As Bayer stressed in his article, his theory gives only qualitatively, how the quadrupolar relaxation occurs in molecular crystals, and is not to be taken too seriously. And we should say that it is rather surprising that such a simple model gives a reasonable value of τ_a and can predict the general feature of temperature dependence of T_1 though qualitatively. But if we desire a more quantitative agreement between the theoretical and the experimental values, the theory of the quadrupolar relaxation must be reconstructed*.

The author would like to express his sincere thanks to Professor I. Takahashi for his continuous interest and discussions. The author's thanks are also due to members of his laboratory for their assistances in construction of the apparatus and in measurements.

References

- 1) W. G. Proctor and W. H. Tanttilla: *Phys. Rev.* **10** (1956) 1757. D. E. Woessner and H. S. Gutowsky: *J. Chem. Phys.* **27** (1957) 1072. T. Hashi: *J. Phys. Soc. Japan* **13** (1958) 911.
- 2) H. Bayer: *Z. Physik* **130** (1951) 227.
- 3) See e.g. T. P. Das and E. L. Hahn: *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc., New York, 1958) 39.
- 4) T. Hashi, A. Hirai, M. Sasaki, and T. Kawai: *Memoir of the College of Science, University of Kyoto, Series A*, **29** (1959) 205.
- 5) B. D. Saksena: *J. Chem. Phys.* **18** (1950) 1653.

* Although Proctor and Tanttilla¹⁾ mentioned in their article that the temperature dependence of T_1 of Cl^{35} in NaClO_3 could be satisfactorily explained by Chang's theory, which seems to be an extension of Van Kranendonk's theory (*Physica* **20** (1954)) 781 on the quadrupolar relaxation in ionic crystals in N.M.R., yet we could not compare our results with Chang's theory, since it was impossible to obtain his article from University of Washington.

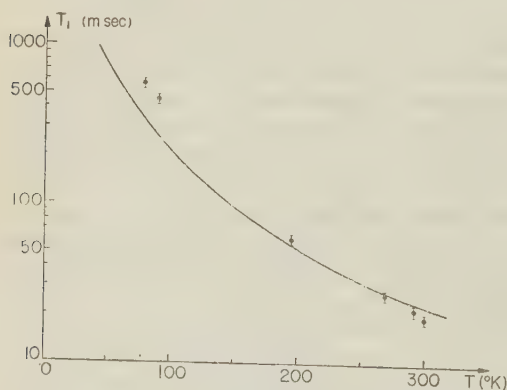


Fig. 1. Theoretical curve and experimental points of T_1 of Cl^{35} in para-dichlorobenzene.

J. PHYS. SOC. JAPAN **15** (1960) 203**Synthesis of AlN Crystals**

Tetsuo MATSUMURA and Yasaku TANABE

*Research Institute for Scientific Measurements,
Tohoku University, Sendai, Japan*

(Received November 26, 1959)

The present experiment is the first step in a series of experiments carried out in anticipation of possibility of electroluminescence in AlN single crystal. Luminescence of AlN¹⁾ and electroluminescence of BN²⁾ in which B has the similar electronic configuration to Al are evidences that justify our anticipation. As the method of synthesizing AlN crystals from melt is difficult because of its high melting point (2200°C, 4 atm.), we tried to synthesize AlN crystals by Frerichs' and sublimation methods, which we had used in making ZnS and CdS crystals³⁾.

Experimental arrangements are shown in Fig. 1.

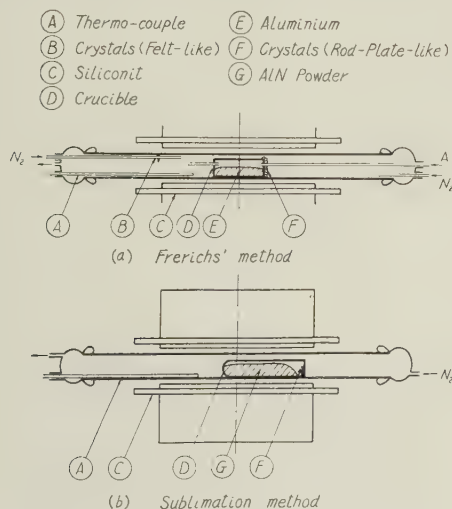


Fig. 1. Experimental arrangement for crystal growth.

(1) Frerichs' method:

After the NC crucible had been filled with pure Al, it was inserted in the combustion tube. Argon gas was introduced to the crucible as carrier gas and N₂ gas was passed into the combustion tube. The tube was then heated to 1500°C at which it was kept for 24 hours. Al vapour was carried off from the crucible and reacted with N₂. AlN crystals grew on the wall of the combustion tube at temperature suitable for their growth. Fine pale-gray colored crystals grew thickly at 1020°C, gradient 70°C/cm. They looked like felt and were as elastic as felt. Transparent, colorless rod- and plate-like crystals grew at 1450°C, gradient 15°C/cm. Rod-like crystals up to 4×0.1×0.1 mm and

plate-like crystals about 1 mm² were obtained.

Typical rod-like crystals are shown in Photo 1.

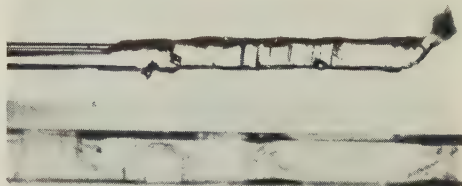


Photo. 1. Rod-like crystals.

They have striations perpendicular to the long direction of the crystals. These crystals often show hexagonal patterns. The growth direction is [10,0] or [11,0].

Photo. 2 shows a plate-like crystal.

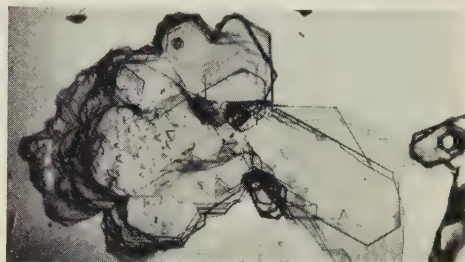


Photo. 2. Plate-like crystal.

It has many regular triangles and hexagons (vertex angle 120°) on it. The crystal grows in layers along the direction perpendicular to the c-axis.

(2) Sublimation method:

SSA crucible filled with AlN powder made by chemical reaction at 1000°C was inserted in the NC combustion tube, as shown in Fig. 1 (b). N₂ gas was passed into the system and the tube was heated to 1500°C. After 24 hours, rod-like crystals smaller than those obtained by method (1) were obtained in the crucible at 1200°C, gradient 70°C/cm.

In general, 1500°C is too low a temperature to synthesize large crystals of AlN. We are now improving the apparatus and the method to carry on experiments in a series.

References

- 1) E. Tiede, M. Thimann and K. Sensse: Chem. Ber. **61** (1928) 1568.
- 2) S. Larach and R. Shrader: Phys. Rev. **104** (1956) 68.
- 3) T. Matsumura, H. Fujisaki and Y. Tanabe: Sci. Rep. RITU, **10** (1958) 459.

J. PHYS. SOC. JAPAN **15** (1960) 204

Crystal Growth of CdS in the Vertical Furnace

Haruo FUJISAKI and Yasaku TANABE

Research Institute for Scientific Measurements,
Tohoku University, Sendai, Japan

(Received November 26, 1959)

For the purpose of improving the techniques of the sublimation method¹⁾⁻⁴⁾ for growing single crystals of CdS and of studying its growth mechanism, experiments were carried out in a vertical furnace. The convection and diffusion of CdS vapor were studied closely.

The furnace shown in Fig. 1 was heated by

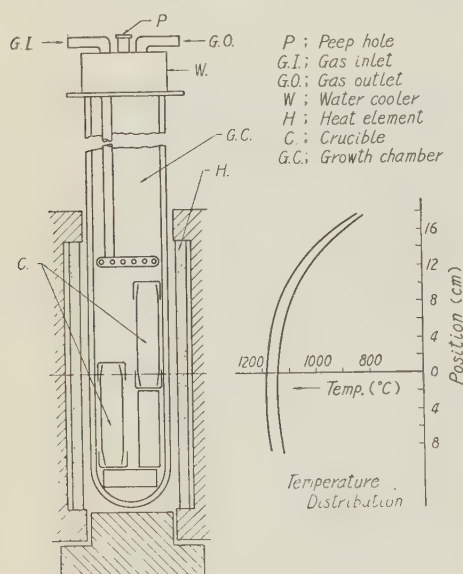


Fig. 1. Vertical furnace with growth chamber and its temperature gradient.

vertical bar-type heat elements circularly distributed. Silica tube 75 mm across and 55 cm long was used for a growth chamber. The two crucibles of fused quartz tube 25~30 mm across and 120 mm long with two caps at both ends were charged with luminescent pure CdS powder, or with pressed tablets (15 mm across) of CdS powder. One crucible was so placed that its bottom was in the middle part of the furnace and the other crucible was set up so that its top was in the middle part of the furnace. The growth chamber was evacuated and kept at 250~300°C for 2~3 hours. Then the temperature of the furnace was raised to 1100~1150°C and kept for 24~48 hours. At the places having a steep temperature gradient the crystals grow on the crystal nucleus. The nuclei of crystals were those which were the new crystals condensed from CdS vapor phase and those crystalites which were

produced by recrystallization from CdS powder.

Examples of crystals obtained are shown in Photo.

1. The crystals deposited on the top and the bottom of the crucible are shown in (a) and (b) respectively. The crystal developed on the inner wall of

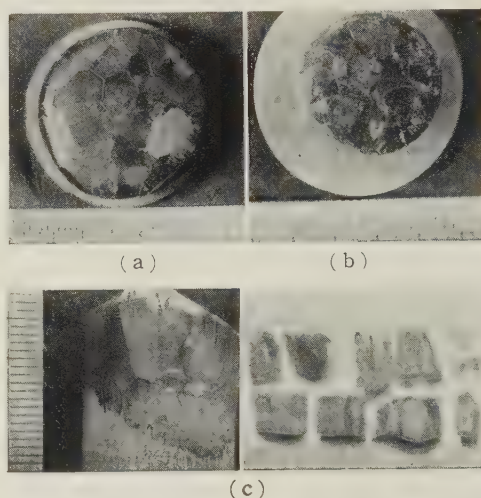


Photo. 1. CdS crystals grown by sublimation method in the vertical furnace. (Scale; 1 mm per division).

- (a) Mosaic growth on the top substrate of the crucible.
- (b) Mosaic growth on the bottom substrate.
- (c) Polycrystalline growth along the inside wall of the crucible.

the cylindrical crucible is shown in (c). They were of mosaic structure having boundaries formed by several single crystals.

It was found by microscopic observation that there were traces of growth layer steps, striations of thermal etch patterns and rows of micro-crystals showing dendrite structure in the growth front surfaces. These surface structures are influenced by temperature, temperature gradient of the growth place and the cooling velocity of the furnace.

These results show that large single crystals of CdS can be obtained in a shorter time interval by heat treatment in the vertical furnace and that the behavior of layer growth⁵⁾ plays an important role in the mechanism of crystal growth.

A detailed description will be published later.

References

- 1) L. C. Greene, D. C. Reynolds, S. J. Czyzak and W. M. Baker: *J. Chem. Phys.* **29** (1958) 1375.
- 2) D. R. Boyd and Y. T. Sihvonen: *J. Appl. Phys.* **30** (1959) 176.
- 3) J. Nishimura and Y. Tanabe: *J. Phys. Soc. Japan* **14** (1959) 850.
- 4) S. Ibuki: *J. Phys. Soc. Japan* **14** (1959) 1181.
- 5) D. C. Reynolds and L. C. Greene: *J. Appl. Phys.* **29** (1958) 559.

J. PHYS. SOC. JAPAN **15** (1960) 205~206

Dislocations in Si Single Crystals

By Takashi FURUOYA and Yozo SASAKI

Research Laboratory, Nippon Electric Co., Ltd., Kawasaki

(Received December 3, 1959)

Dash¹⁾ has reported on the processes of occurrence and disappearance of dislocations in Si single crystals. In the present note we will report some additional phenomena on the behavior of dislocations observed in pulled Si single crystals.

The crystals were pulled from quartz crucibles along $\langle 111 \rangle$ axis by the Teal-Little method. The rotation and the pulling rate were 3~6 r.p.m. and 0.2~2 mm/min., respectively. Slices were cut from the crystals parallel to the pulling axis and also to (110) plane, and were decorated with Cu. A photograph taken by use of an infra-red image tube is given in Fig. 1. The interface between the seed and the pulled crystal is indicated by the arrow (1). After the seed had been dipped into the Si melt, the density of dislocation in the seed was examined by the method of etch pit density and was found to have increased appreciably up to $10^3 \sim 10^4/\text{cm}^2$. Then the crystal was pulled at a low pulling rate (0.2 mm/min.) for about 5 minutes. The dislocation density in this period was $10^3 \sim 10^4/\text{cm}^2$ and did not decrease appreciably. Then the crystal was pulled at a higher rate (about 1 mm/min.). All the dislocation disappeared in 15~20

minutes. A process of the disappearance of dislocation is reported by Dash¹⁾, viz., dislocations propagate to the crystal surface and disappear. This process is illustrated in Fig. 2a. There is another possible process of disappearance, in which two

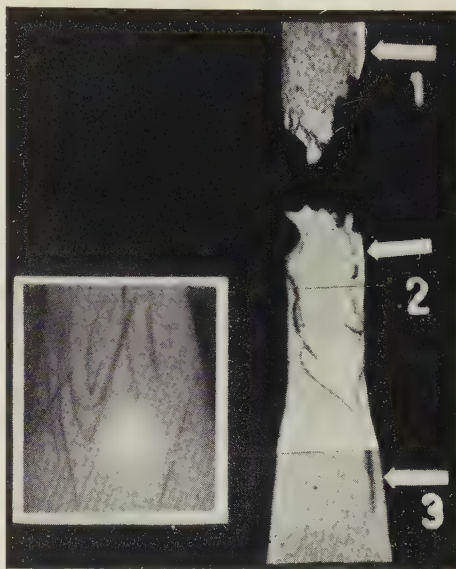
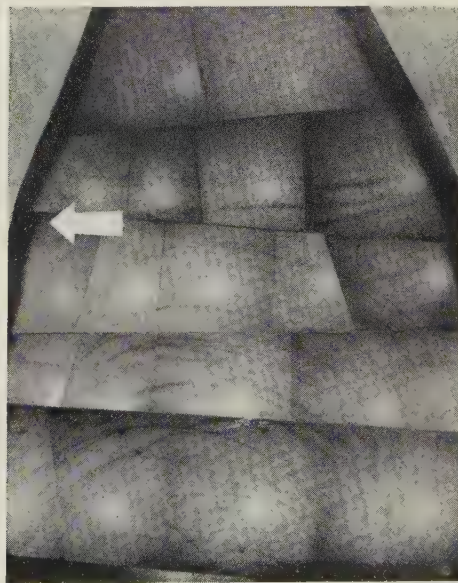


Fig. 1. The disappearance of two screw dislocations having opposite signs by combination is illustrated by the arrow (3) and also in the inset. The sample was broken in handling after Cu decoration, then pieced together, resulting in the dark area.



(a)



(b)

Fig. 2. Three dislocations propagating to the surface (a) and dislocation loops by the slip of dislocations (b).

screw dislocations having opposite signs combine each other in the course of propagation. The disappearance of dislocations in the latter process is indicated in Fig. 1 by the arrow (3) and also in the inset in it.

The pattern dotted with decorated Cu, which is indicated by the arrow (2), would correspond to a helical dislocation. Helical dislocations were observed by Bontinck and Amelinckx²⁾ in fluorite crystals, and it was suggested by Weertman³⁾ that the form of dislocation lines in equilibrium under the ordinary stress induced by the deviation of the vacancy (or interstitial atom) concentration from the equilibrium value was helical.

Effect of thermal shock on dislocations is shown in Fig. 2b. The temperature of Si melt was suddenly raised at the time indicated by the arrow. Many large dislocation loops developed. They were probably results of slip of dislocations, which had occurred in (111) plane perpendicular to the growth direction. It is interesting to note that the dislocation loops emerged only when the temperature of the Si melt was raised, and didn't when the temperature was lowered.

The authors wish to thank Dr. Y. Ishikawa for his continual encouragements, and they are also indebted to Dr. E. Matsuura for his valuable discussions.

References

- 1) W. C. Dash: J. Appl. Phys. **30** (1959) 459.
W. C. Dash: *Growth and Perfection of Crystals* (John Wiley & Sons, 1958) 361.
- 2) W. Bontinck and S. Amelinckx: Phil. Mag. **2** (1957) 94.
- 3) J. Weertman: Phys. Rev. **107** (1957) 1259.

J. PHYS. SOC. JAPAN **15** (1960) 206~207

Observation of Layer Structure in Dislocation Free Silicon Crystals with the Use of X-ray Anomalous Transmission

By Zensho ISHII,

Electrotechnical Laboratory, Nagatacho, Tokyo

Takashi FURUOYA, Yozo SASAKI

Research Laboratory, Nippon Electric Co. Ltd., 1753, Shimonumabe, Kawasaki

and Kazutake KOHRA

Institute of Physics, College of General Education, University of Tokyo, Komaba, Meguro-ku, Tokyo

(Received November 17, 1959)

The layer structure in the Si single crystals free from dislocations was observed by Dash¹⁾ by the

method of Cu decoration. The present note reports that this structure can be also observed by X-rays with the use of anomalous transmission, without decorating the specimen with Cu.

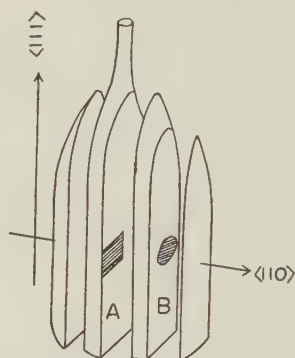


Fig. 1. Schematic diagram of specimens cut from the pulled Si single crystal.

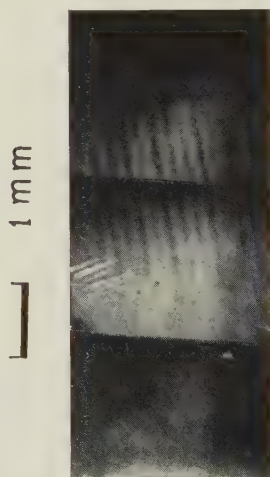


Fig. 2. Photograph by the infra-red image tube of the hatched region of the slice A in Fig. 1.



Fig. 3. X-ray transmission photograph of the slice B in Fig. 1.

Si single crystals were pulled along the $\langle 111 \rangle$ axis from quartz crucibles by the Teal-Little method. The rotation and pulling rates were 6 r.p.m. and 1 mm per min., respectively. From one of the crystals slices parallel to the $(1\bar{1}0)$ plane were cut out (Fig. 1). The surfaces of the slices were carefully lapped and etched with the $3\text{HNO}_3 + 1\text{HF}$ solution. The final thickness of the slices was about 1 mm.

One of the slices (A in Fig. 1) was decorated with Cu^{2+} and observed by an infra-red image tube from the direction normal to the surface. A photograph taken is given in Fig. 2. In this photograph no dislocation line was observed, while the layer structure, reported by Dash, was observed clearly.

Another slice (B in Fig. 1), located adjacent to the slice (A), was observed by the transmission method of X-rays³⁾, where the parallel beam of $\text{CuK}\alpha^{4),5)}$ was used. The specimen was set so that the $(\bar{2}20)$ reflexion was excited. As shown in Fig. 3, the layer structure similar to that shown in Fig. 2 was observed, but the dislocation line was absent.

The period of the layer structure was approximately 0.18 mm in Fig. 2 and 0.20 mm in Fig. 3. The widths of the dark and white layers were 0.08 and 0.10 mm, respectively, in Fig. 2 and were 0.07 and 0.13 mm in Fig. 3. Coincidence between the Fig. 2 and Fig. 3 were satisfactory. The value of the period would correspond to the amount of the material withdrawn in one revolution, the latter being about 0.17 mm. The dark layer in Fig. 3 is the region where the X-ray intensity is weaker, and accordingly the lattice structure of the region is more distorted. Such a distortion may probably be due to the accumulation of oxygen or vacancy clusters according to Dash.

The X-ray method will be a convenient one for studying such lattice defects because it does not damage the object.

References

- 1) W. C. Dash: J. Appl. Phys. **30** (1959) 459.
W. C. Dash: *Growth and Perfection of Crystals*. (John Wiley and Sons, 1958) 361.
- 2) W. C. Dash: J. Appl. Phys. **27** (1956) 1387.
- 3) G. Borrmann, W. Hartwig and H. Irmeler: Z. Naturforsch. **13a** (1958) 423.
- 4) H. Barth and R. Hosemann: Z. Naturforsch. **13a** (1958) 792.
- 5) Z. Ishii and K. Kohra: J. Phys. Soc. Japan **14** (1959) 1250.

J. PHYS. SOC. JAPAN **15** (1960) 207~208

Intervalley Scattering of Hot Electrons

By Motoichi SHIBUYA and Wataru SASAKI

Electrotechnical Laboratory, Tokyo, Japan

(Received October 24, 1959)

Electron temperature approximation proposed by Shockley¹⁾ in his discussion of hot electrons is here modified to include the intervalley lattice scattering which is important in a many-valley semiconductor²⁾. At high electric field the electron temperature of the i th valley T_i becomes different from those of other valleys when the directions of the principal axes of the effective mass tensor are different in each valley. Even in neglecting both the optical mode scattering and the intervalley scattering, this results in spanning of a finite angle between the current and the field vectors³⁾. But the experimental studies⁴⁾ seem to show clearly the effect of the intervalley scattering. Qualitative discussions have already been done on a simple model in the earlier papers⁴⁾, so the fundamental equations based on that model and some results deduced from them are briefly outlined here.

The steady state condition for the density of electrons in each valley,

$$dN_i/dt=0, \quad (i=1, 2, \dots, \delta),$$

should be needed in a many-valley semiconductor. From this condition, the product of the electron density N_i and the intervalley collision frequency $\langle v^2 \rangle_i$ becomes independent of the index i . That is, the higher the valley temperature the less the electron density in it. This makes the angle between the field and the current vectors larger.

The steady state condition for the average energy of electrons in each valley becomes a little different from Shockley's because of the intervalley scattering. The loss term due to this is composed of two components; the one, which concerns with the energy given to the lattice, is quite similar to the term due to the optical mode scattering, and the other is a new face due to the electron transfer between the valleys which reduces the differences between the valley temperatures and explains the existence of maximum in the deviation angle versus field curve. Thus the equations to be solved for getting the valley temperatures are following

$$d\langle W \rangle_i/dt = F_i + A_i + O_i + I_i = 0, \quad (i=1, 2, \dots, \delta),$$

where F_i , A_i , O_i and I_i are the terms due to field, acoustic scattering, optical scattering and intervalley scattering,

$$\vec{F}_i = q\vec{E} \parallel \mu_i \parallel \vec{E},$$

$$A_i = \frac{4c^2}{3} \text{Trace} \parallel m_i \parallel \left\{ 1 - \frac{T_i}{T} \right\} \langle v^4 \rangle_i,$$

$$O_i = -\hbar\omega_0 \tanh\left(\frac{\hbar\omega_0}{2kT} - \frac{\hbar\omega_0}{2kT_i}\right) \langle v^0 \rangle_i,$$
$$I_i = -\hbar\omega_I \tanh\left(\frac{\hbar\omega_I}{2kT} - \frac{\hbar\omega_I}{2kT_i}\right) \langle v^I \rangle_i$$
$$- \frac{\langle v^I \rangle_i}{(\delta-1)} \sum_{j \neq i} \{\gamma_i k T_i - \gamma_j k T_j\},$$

and

$$\|\mu_i\| = q \|m^{-1}\| \frac{\langle \tau W \rangle_i}{\langle W \rangle}$$

is the mobility tensor of the electrons in the i th valley. The symbol $\langle f \rangle_i$ is used for the Boltzmann average of f in the electron temperature approximation and v^a is the collision frequency of the a th kind. γ_i is a complicated but slow varying function of T_i , having the numerical value of the order of 1.

Computing the valley temperatures which satisfy the above equations, the drift velocity can be finally evaluated by

$$\vec{v}_d = \sum_i N_i \|\mu_i\| \vec{F} / \sum_i N_i.$$

Some results obtained from this formulation for n -type Ge at room temperature are shown in Fig. 1, assuming $\mu_0(300^\circ\text{K})=3600\text{ cm}^2/\text{volt sec}$, $c=5\text{ km/}$

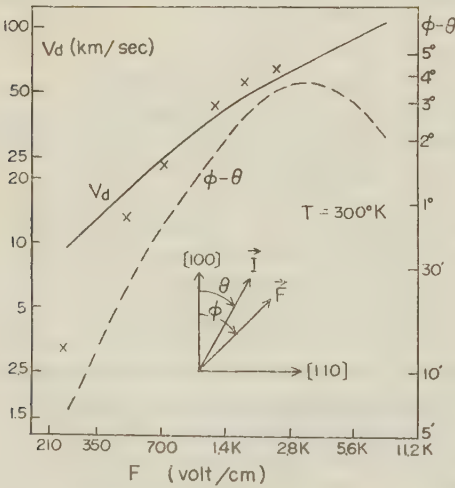


Fig. 1. The calculated $|\vec{v}_d| \sim |\vec{F}|$ and $(\varphi-\theta) \sim |\vec{F}|$ curves are plotted in solid and broken lines, assuming $\varphi=30^\circ$. Observed values of $(\varphi-\theta)$ at $\theta=30^\circ$ are also plotted with cross marks.

sec, $w_0/w_A=0.2$, $w_I/w_A=0.02$, $\hbar\omega_0=430^\circ k$, $\hbar\omega_I=330^\circ k$ and $\delta=4$. The $|\vec{v}_d|$ versus $|\vec{F}|$ curve and $(\varphi-\theta)$ versus $|\vec{F}|$ curve are plotted with solid and broken lines, when the field vector lies in (110) plane with the angle $\varphi=30^\circ$ from the [100] axis. The experimental data of $(\varphi-\theta)$ when the current vector lies in the same plane with the angle $\theta=30^\circ$ from the same axis are plotted with cross marks

for comparison. Agreement between both results is quite satisfactory. The highest and the lowest valley temperatures are, in this case, 1000°K and 600°K at the electric field where $(\varphi-\theta)$ curve shows maximum.

The derivation of these equations and the whole results computed for n -type Ge at room, dry ice and oxygen temperatures will be published soon elsewhere.

References

1) W. Shockley: Bell Syst. Tech. J. **30** (1951) 990.
2) C. Herring: Bell Syst. Tech. J. **34** (1955) 237.
3) M. Shibuya: Phys. Rev. **99** (1955) 1189.
4) W. Sasaki and M. Shibuya: J. Phys. Soc. Japan **11** (1956) 1202. W. Sasaki, M. Shibuya and K. Mizuguchi: J. Phys. Soc. Japan **13** (1958) 456. W. Sasaki, M. Shibuya, K. Mizuguchi and G. M. Hatoyama: J. Phys. Chem. Solids **8** (1959) 250.

J. PHYS. SOC. JAPAN **15** (1960) 208~209

On the Quasi-two-dimensional Laminar Boundary Layer

By Nisiki HAYASI

Transportation Technical Research Institute,
Mitaka, Tokyo

(Received November 6, 1959)

Using a normal coordinate system¹⁾ x, y, z whose scale factors are A, B and C , and in which $z=0$ gives a body surface, we consider the compressible laminar boundary layer on that surface. Let (u, v, w) be the components of the velocity in the directions of x, y, z increasing, ρ the density, p the pressure, t the time, μ the coefficient of viscosity, k the thermal conductivity, T the temperature, and I the enthalpy. Then, assuming $\partial A/\partial z = \partial B/\partial z = O(1)$, the boundary-layer equations for a perfect gas are

$$\partial(\rho B C u)/\partial x + \partial(\rho C A v)/\partial y + \partial(\rho A B w)/\partial z = 0, \tag{1}$$

$$Du + \frac{v}{AB} \left(u \frac{\partial A}{\partial y} - v \frac{\partial B}{\partial x} \right) = - \frac{1}{\rho A} \frac{\partial p}{\partial x} + \frac{1}{\rho C} \frac{\partial}{\partial z} \left(\frac{\mu}{C} \frac{\partial u}{\partial z} \right), \tag{2}$$

$$Dv - \frac{u}{AB} \left(u \frac{\partial A}{\partial y} - v \frac{\partial B}{\partial x} \right) = - \frac{1}{\rho B} \frac{\partial p}{\partial y} + \frac{1}{\rho C} \frac{\partial}{\partial z} \left(\frac{\mu}{C} \frac{\partial v}{\partial z} \right), \tag{3}$$

$$O(1) = \partial p / \partial z, \tag{4}$$

$$\rho DI - Dp = \frac{\mu}{C^2} \left\{ \left(\frac{\partial u}{\partial z} \right)^2 + \left(\frac{\partial v}{\partial z} \right)^2 \right\} + \frac{1}{C} \frac{\partial}{\partial z} \left(\frac{k}{C} \frac{\partial T}{\partial z} \right), \quad (5)$$

where

$$D = \frac{\partial}{\partial t} + \frac{u}{A} \frac{\partial}{\partial x} + \frac{v}{B} \frac{\partial}{\partial y} + \frac{w}{C} \frac{\partial}{\partial z}.$$

We choose the x -axis along the streamline of the external flow evaluated on the surface, assuming that this streamline is not moving, and the y -axis along the orthogonal trajectory to the said streamline. Then, at the outer edge of the boundary layer, $u=U$ and $v=0$, so that from (3),

$$U^2 \Gamma = (\partial p / \partial y) / \rho B, \quad (6)$$

where $\Gamma = (\partial A / \partial y) / AB$ is the geodesic curvature of the streamline. Since we have assumed that $\partial A / \partial z = \partial B / \partial z = O(1)$, $\partial \Gamma / \partial z = O(1)$, so that Γ is approximately equal to the geodesic curvature of the x -axis. When the body surface is solid and not moving, the boundary conditions for v are $v=0$ at $z=0$ and $z \rightarrow \infty$. If the x -axis is a geodesic of the surface, $\Gamma=0$ there, so that throughout the boundary layer, $\Gamma=O(\delta)$, where δ is the boundary-layer thickness. Then we have, from (6), $\partial p / \partial y = O(\delta)$ at the outer edge of the boundary layer. Hence considering $\partial p / \partial z = O(1)$, we see that $\partial p / \partial y = O(\delta)$ throughout the boundary layer. Therefore $v=0$ is a solution of Eq. (3). In such a case, the boundary-layer flow may be called 'quasi-two-dimensional'²⁾. On the other hand, if $v=0$, Eq. (3) gives $\Gamma u^2 = (\partial p / \partial y) / \rho B$. Therefore $\Gamma \partial(\rho u^2) / \partial z = O(1)$. Since $\partial(\rho u^2) / \partial z = O(\delta^{-1})$, we have $\Gamma = O(\delta)$. Thus $\Gamma = O(\delta)$ is the necessary and sufficient condition for the boundary layer to be quasi-two-dimensional, when $\partial A / \partial z = \partial B / \partial z = O(1)$. For the quasi-two-dimensional flow, Eqs. (2), (3), (4) and (5) are reduced respectively to

$$\frac{\partial u}{\partial t} + \frac{u}{A} \frac{\partial u}{\partial x} + \frac{w}{C} \frac{\partial u}{\partial z} = -\frac{1}{\rho A} \frac{\partial p}{\partial x} + \frac{1}{\rho C} \frac{\partial}{\partial z} \left(\frac{\mu}{C} \frac{\partial u}{\partial z} \right), \quad (7)$$

$$\frac{\partial p}{\partial y} = O(\delta), \quad \frac{\partial p}{\partial z} = O(1), \quad (8)$$

$$\rho \left(\frac{\partial I}{\partial t} + \frac{u}{A} \frac{\partial I}{\partial x} + \frac{w}{C} \frac{\partial I}{\partial z} \right) - \frac{\partial p}{\partial t} - \frac{u}{A} \frac{\partial p}{\partial x} = \mu \left(\frac{1}{C} \frac{\partial u}{\partial z} \right)^2 + \frac{1}{C} \frac{\partial}{\partial z} \left(\frac{k}{C} \frac{\partial T}{\partial z} \right). \quad (9)$$

Without loss of generality, we may take $C=1$. Then Eq. (1) reduces to

$$\frac{1}{A} \frac{\partial}{\partial x} (\rho B u) + \frac{\partial}{\partial z} (\rho B w) = 0. \quad (10)$$

Since $\partial B / \partial z = O(1)$, we can replace B by B_0 , where $B_0 = B(x, y, 0)$. Then after the coordinate transfor-

mation $X = \int_0^x A dx$, Eqs. (7), (8), (9) and (10) are reduced to the equations similar to those of the axisymmetric boundary layer. Therefore Mangler³⁾-Hatanaka⁴⁾ transformations

$$\xi = \int_0^x B_0^2 dx, \quad \zeta = B_0 z, \quad u = u^*,$$

$$w = B_0 w^* - zu(\partial B_0 / \partial X) / B_0$$

reduce them to the equations similar to those of the two-dimensional boundary layer

$$\partial(\rho u^*) / \partial \xi + \partial(\rho w^*) / \partial \zeta = 0,$$

$$\frac{\partial u^*}{\partial t} + u^* \frac{\partial u^*}{\partial \xi} + w^* \frac{\partial u^*}{\partial \zeta} = -\frac{1}{\rho} \frac{\partial p}{\partial \xi} + \frac{1}{\rho} \frac{\partial}{\partial \zeta} \left(\mu \frac{\partial u^*}{\partial \zeta} \right),$$

$$\frac{\partial p}{\partial y} = O(\delta), \quad \frac{\partial p}{\partial \zeta} = O(1),$$

$$\rho \left(\frac{\partial I}{\partial t} + u^* \frac{\partial I}{\partial \xi} + w^* \frac{\partial I}{\partial \zeta} \right) - \frac{\partial p}{\partial t} - u^* \frac{\partial p}{\partial \xi} = \mu \left(\frac{\partial u^*}{\partial \zeta} \right)^2 + \frac{\partial}{\partial \zeta} \left(k \frac{\partial T}{\partial \zeta} \right).$$

Crocco⁵⁾ and Busemann^{6),7)} have shown that when specific heat at constant pressure c_p is constant and Prandtl number ($=\mu c_p / k$) is equal to unity, the equations of motion and of energy for steady two-dimensional boundary layer coincide if $T_H = T_w + Ku$ and $K \partial p / \partial x = 0$, where K is a constant, $T_H = T + u^2 / (2c_p)$ and T_w is the constant temperature at the wall. Clearly this is also valid for steady quasi-two-dimensional boundary layer. Indeed, from (2), (3), and (5), it can be shown that $T_H = T_w$ is a specific integral for steady three-dimensional boundary layer, where $T_H = T + (u^2 + v^2) / (2c_p)$.

References

- 1) R. Sedney: Q. Appl. Math. **15** (1957) 113.
- 2) N. Hayasi: to be published in this journal.
- 3) W. Mangler: Z. A. M. M. **28** (1948) 97.
- 4) H. Hatanaka: Rep. Inst. Sci. Technol. Univ. Tokyo **3** (1949) 115.
- 5) L. Crocco: L'Aerotecnica **12** (1932) 181; also N. A. C. A. Tech. Memo. no. 690 (1932).
- 6) A. Busemann: Handbuch d. Exp.-phys., Bd. 4, Teil 1. (Akademische Verlagsgesellschaft, Leipzig, 1931) s. 366.
- 7) A. Busemann: Z. A. M. M. **15** (1935) 23.

J. PHYS. SOC. JAPAN 15 (1960) 210~211

Magnetic Property of $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$

By Kiiti SIRATORI and Shuichi IIDA

*Department of Physics, Faculty of Science,
University of Tokyo, Tokyo, Japan*

(Received November 13, 1959)

Chromium dioxide is the only simple oxide in which dominant superexchange interaction is clearly ferromagnetic. Guillaud et al.¹⁾ concluded that the saturation magnetization is $2.07(\pm 0.03)\mu_B$ per Cr^{4+} ion. But the specimens they used were considerably impure containing about 40-50% Cr_2O_3 .

In order to make the nature of magnetic interaction in CrO_2 clearer, the magnetic property of solid solution $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$ was studied. MnO_2 is known to be antiferromagnetic below 84°K^2 .

Specimens were prepared by heating the powdered mixture of MnO_2 and CrO_3 which was made from Mn nitride and CrO_3 by heating it up to about 150°C in air, up to $400\text{--}550^\circ\text{C}$ in atmosphere of 100 Kg/cm^2 oxygen. Oxygen content of the specimens was determined from the weight change induced after heating them up to 1350°C in air. They all lie between $\text{Mn}_x\text{Cr}_{1-x}\text{O}_{1.98}$ and $\text{Mn}_x\text{Cr}_{1-x}\text{O}_{2.05}$.

The X-ray diffraction patterns by Norelco diffractometer show that this system has a solidus immiscibility range near MnO_2 . Presence of two phases, each of which has rutile type crystal structure, was observed in the specimens of $x = 0.75, 0.8, 0.85$. The lattice constant vs. proposed composition x is shown in Fig. 1. Scattering in the

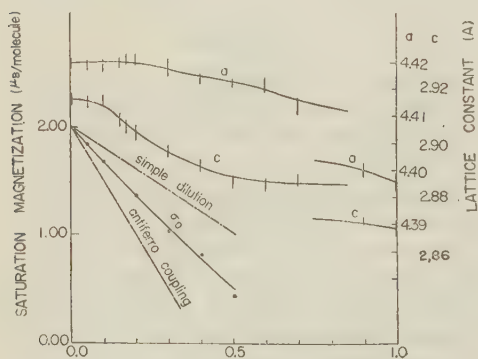


Fig. 1. Lattice constant at room temperature and saturation magnetization at 0°K of $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$.

value of lattice constant of the specimens at fixed x , which will be due to the change of oxygen content, is within the error of the X-ray analysis. Variation of c shows two anomalies, origin of which has not yet been made clear.

Magnetic measurements were carried out with pendulum type magnetometer. The results are

shown in fig. 2. The sensitivity of the apparatus is about 1 gauss/gr, and probable error may amount

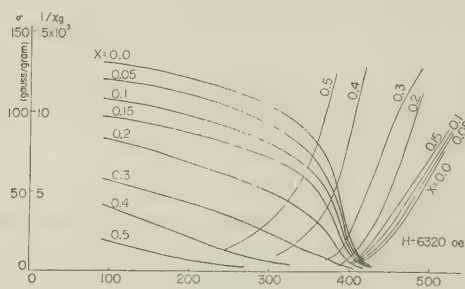


Fig. 2. Thermomagnetic curves of $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$.

to 2-3%. As the sensitivity of the apparatus is not so high, paramagnetic susceptibility was measured only in limited temperature range. Therefore, except for the specimens with small x , the measurements were not performed to so high a temperature range as to show a linear relationship in $1/\chi$ - T curves.

Extrapolated values of saturation magnetization at 0°K are shown in Fig. 1. They lie between the broken line and the chain line. The broken line represents the magnetization calculated from the assumption that magnetic moment of Cr^{4+} and Mn^{4+} is $2\mu_B$ and $3\mu_B$ per ion respectively and that all the magnetic moments of Mn ions couple antiferromagnetically with those of Cr ions, which are aligned ferromagnetically. The chain line represents the results expected when the magnetization of CrO_2 is simply diluted by the addition of MnO_2 . Our results may be accounted for by an antiferromagnetic interaction between Cr^{4+} and Mn^{4+} . The deviation from the broken line may probably be due to the antiferromagnetic coupling between Mn ions themselves. If we assume that Mn and Cr ions are mixed completely, this leads to a conclusion that $\text{Mn}^{4+}\text{--Mn}^{4+}$ interaction must be stronger than $\text{Mn}^{4+}\text{--Cr}^{4+}$ interaction. However it is also probable, that the mixing is not complete, as the firing temperature is not so high. In some cases, magnetic property of the specimen fired for 50 hours is different from that of the specimen fired for 100 hours. The data shown in Fig. 2 are of those specimens which are considered to show no appreciable change by further firing.

In a region of small x , the variation of Curie constant with x is consistent with the above assumption about the magnetic moment of two ions.

When x is smaller than 0.2, ferromagnetic Curie temperature does not vary appreciably. So it seems that Cr-Mn interaction is as strong as Cr-Cr interaction in this crystal.

The obtained value of saturation magnetization of CrO_2 is $2.00\mu_B/\text{ion}$, but estimated composition of this specimen is $\text{CrO}_{1.99}$ and trace of Cr_2O_3 has been discovered with X-ray analysis. Therefore,

if we assume that all the Cr^{3+} ions are present in form of Cr_2O_3 , saturation magnetization of CrO_2 should be $2.04\mu_B/\text{ion}$. Theoretically, the presence of the value larger than 2.00 is difficult to interpret, but the value obtained by Guillaud was also larger than 2.

References

- 1) P. C. Guillaud, A. Michel, J. Bénard and M. Fallot: *Compt. rend.* **219** (1944) 58.
- 2) H. Bizette: *J. Phys. radium* **12** (1951) 161.

J. PHYS. SOC. JAPAN **15** (1960) 211

Formation Mechanism of F-Centers in KCl Single Crystal Heated in Potassium Vapor

By HIROYUKI MIZUNO and MORIO INOUE
Matsushita Electronics Corporation,
Takatsuki

(Received November 10, 1959)

A KCl crystal grown from melt by Kyropoulos method was heated to form F-centers exposing only one surface to potassium vapor at 500°C for 14 hours. Assuming the oscillator strength as 0.81, the mean number of F-centers in the original crystal was derived from the absorption coefficient and band width. The absorption coefficient of the colored crystal was measured again after its exposed surface was polished about 30 to 100 microns with iron oxide ferric (red ochre). This process was repeated to the depth of 600 microns from the exposed surface. It is natural to suppose that the decrease of the absorption coefficient is attributed to the F-centers contained in the layer scraped off from the crystal. Taking x -axis perpendicular to the exposed surface, the mean number n of F-centers in the scraped layer is easily estimated as below;

$$n = \frac{l - dx}{dx} \{ \bar{C} - \bar{C}_{dx} \} + \bar{C}$$

where l is the thickness of the crystal before scraping, $\bar{C}$ is its number of F-centers, dx is the thickness of scraped layer and $\bar{C}_{dx}$ is the number of F-centers included in the crystal after scraping. In Fig. 1 the number of F-centers, thus determined, is plotted on a logarithmic scale *versus* depth of penetration. The points lie upon a straight line within the experimental error, except one point nearest to the exposed surface. Such irregularity near the surface may be due to excess deposit of potassium. Fisher¹⁾ analyzed the penetration into

a crystal along disordered internal interfaces. Making the assumptions (a) that the interface diffusion is analogous to the heat diffusion along a thin copper foil imbedded in cork and (b) that the diffusion outside the interfaces is initially normal to them, he derived a relation by that which a plot of $\log n$ *versus* depth of penetration should lie on a straight line, whereas in volume diffusion, as well known, a straight relation appears when $\log n$ is plotted as a function of the square of depth. According to Fisher's results it seems reasonable to suppose from the results in Fig. 1

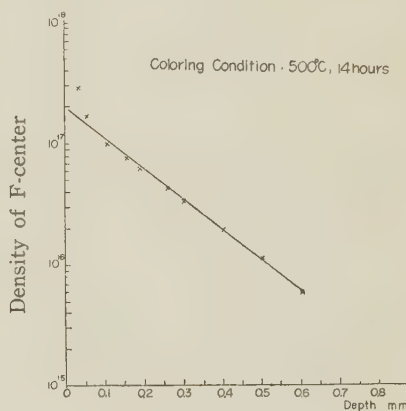


Fig. 1. Density of F-centers *versus* depth for KCl additively colored.

that in the additive coloring of ionic crystals in alkali metal vapor at 500°C the penetration of the metal into crystal may be mainly dependent on the process of disordered interface diffusion. Further investigation of the diffusion process including explanation of surface irregularity and structure of disordered interface is, however, left to future work.

Reference

- 1) J. C. Fisher: *J. Appl. Phys.* **22** (1951) 74.

Three New Isotopes, Co^{63} , Ga^{75} , and As^{81} By Haruhiko MORINAGA, Tokihiro KUROYANAGI, Hidehiko MITSUI
and Katsufusa SHODA*Department of Physics, Tohoku University, Sendai*

(Received November 5, 1959)

Three previously unknown isotopes, Co^{63} , Ga^{75} , and As^{81} were identified from the (γ, p) reactions on natural nickel, germanium, and selenium. Their radiations were investigated with the aid of scintillation spectrometers. Decay characteristics are as follows:

	half-lives	beta-decay energies	gamma-rays
Co^{63}	52 ± 5 sec	3.6 ± 0.2 MeV	No
Ca^{75}	2.0 ± 0.2 min	3.3 ± 0.2 MeV	(0.36) 0.58 MeV
As^{81}	31 ± 2 sec	3.8 ± 0.2 MeV	No

§ 1. Introduction

There are nuclides which are not known but could be produced by the (γ, p) reactions. These nuclides are usually difficult to be produced by other reactions, but investigations employing the (γ, p) reactions are often hindered by low intensities and their short half-lives. Such short-lived isotopes are usually in the neutron excess side of the nuclear chart and have rather high beta-decay energy and their half-lives are fairly safely guessed from conventional nuclear theories. This in turn means that the investigations of such isotopes give a chance to extend the systematics of low lying nuclear states.

In the case like As^{81} which is produced by the (γ, p) reactions, the (γ, n) product from the same parent, Se^{83} , is also radioactive. Such examples can give a good chance for investigators of photoreactions to study both the (γ, p) and (γ, n) reactions on a nuclide. Such studies have not been done extensively. The first thing to do along this line is to fix the decay scheme of these unknown isotopes.

Using an internal bombarding technique recently developed in our laboratory¹⁾, we have been studying such unknown isotopes. Here, we report on the results of our investigations of three previously unknown isotopes, Co^{63} , Ga^{75} , and As^{81} .

 Co^{63}

For producing Co^{63} , we irradiated small pieces of 99.99 percent nickel metal in the internal target of the Tohoku University betatron. After a 1.5 minutes bombardment with 25-MeV bremsstrahlung, an activity with a half-life of an order of one minute was

observed. Since this activity could not be assigned to any known isotope to be produced by photoreactions on nickel and was too strong for being assigned to any impurity, it was suspected that this might belong to Co^{63} . Since Co^{62} , which may be formed from the (γ, np) reaction on Ni^{64} , although in small quantity, is reported to have half-life of 1.6 min²⁾, a bombardment was performed with the bremsstrahlung of 18-MeV maximum energy. The short half-lived activity was still observed. This excludes the assignment of this activity to Co^{62} since this energy is not enough to cause the (γ, np) reaction.

In order to assign the element to which the activity belongs, quick chemical separation of the Co activity was carried by α -nitroso- β -naphthol. A short lived component followed Co, although intensity was not enough to determine the half-life exactly.

Fig. 1, shows one of the decay curves of the activity on nickel metal measured with a G-M counter after a 1.5 min bombardment with the 25-MeV bremsstrahlung. The long component is assigned to 1.65 h Co^{61} and 36 h Ni^{57} . From several measurements, the half-life of this activity was determined to be 52 ± 5 sec.

In order to determine the characteristic of this short lived activity, the beta- and gamma-ray measurement was performed with scintillation spectrometers.

For the measurement of the beta-rays, a plastic scintillator of 2 inches in diameter and 1 inch in thickness was employed and the beta-spectra were recorded with a 100 channel pulse height analyzer. Fig. 2 shows

the Kurie plot of the beta-rays between 40 sec and 160 sec after the 1.5 min bombardment. The high energy component disappears in subsequent measurement. After correcting for the self absorption, the end point energy

was determined as 3.6 ± 0.2 MeV. The low energy component does not decay and is attributed to Co^{61} . This value of the end point energy is in good agreement with the beta-decay systematics which give 3.7 MeV as a decay energy. For calibration, P^{32} , In^{114} , Cu^{63} , and Ag^{113} end points were employed.

Gamma-rays were looked for with the aid of a $1\frac{1}{2} \times 1\frac{1}{2}$ inch NaI(Tl) crystal. Gamma-rays with intensities higher than 10% is implausible to exist.

Cross section ratio for producing Co^{63} and Co^{61} is determined to be ~ 1 from the decay curve.

From these observations, it is certain that this beta-decay is attributed to the decay of Co^{63} . From the shell model, the spin of Co^{63} is expected to be $7/2^-$. From the absence of any strong gamma-ray, the ground state of Ni^{63} , which is considered to be either $3/2^-$ or $5/2^-$ from its decay, must be a $5/2^-$ state. Or, if the $3/2^-$ state is actually the ground state, the $5/2^-$ state must be very close to the ground state. This is consistent with the systematics of the low lying states of odd nickel isotopes since the lighter odd isotopes of Ni has the $3/2^-$ ground state but the above lying $5/2^-$ state comes down as the mass increases. The latter comes quite close to the former even at $A=61$. It is, therefore, natural that the $5/2^-$ state may come down below or very close to the $3/2^-$ state. At $A=65$ ground state spin is probably $5/2^-$.

If the decay takes place mostly to the $5/2^-$ ground state, its log ft value is 5. This is also a proper value to be expected in the decay of this type.

Ga⁷⁶

Among the possible photo-nuclear product nuclides produced by the 25-MeV bremsstrahlung on natural germanium, Ga^{76} is the only unknown isotope as the former case. For producing Ga^{76} , we bombarded extremely pure metallic germanium samples in the similar arrangement. Besides all the known activities a component which decayed with a half-life of approximately 2 minutes was observed. In this case the 49 sec isomer of Ge^{76} is produced in large quantity and disturbs G-M counter measurement for determining the halflife. Therefore, in order to determine the half-life we measured the half-life of

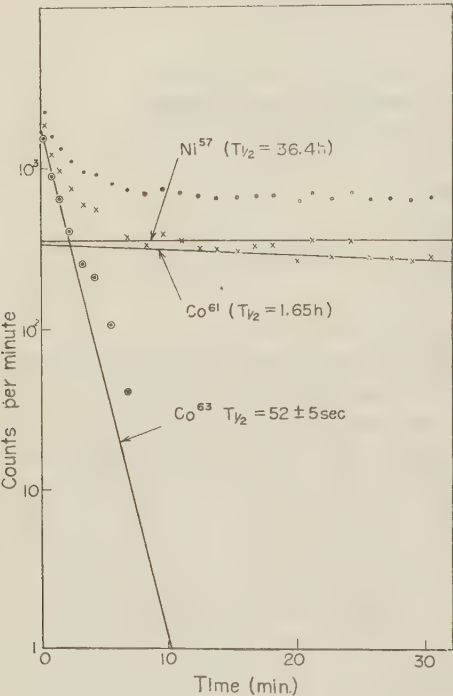


Fig. 1. Decay curve of a Ni sample bombarded for 1.5 min taken with a G-M counter.

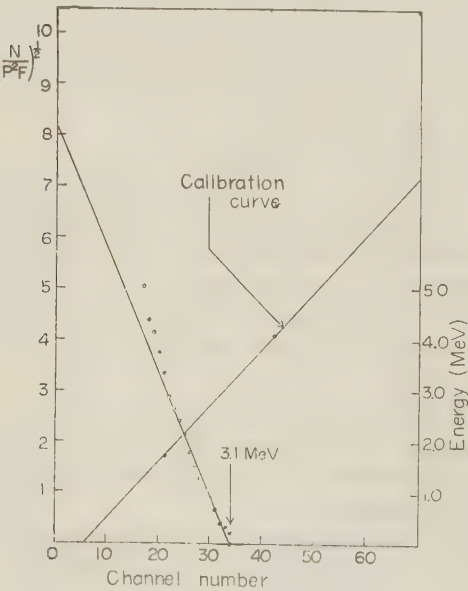


Fig. 2. Kurie plot of beta spectrum of the Co^{63} taken with a plastic scintillator. Self-absorption correction is not applied yet.

radiations which gives larger pulse than 1-MeV electrons in the plastic scintillator. This discrimination is effective to let the short half lived isotope stand out since the new

short lived isotope should have a higher beta decay energy than the longer lived ones. Fig. 3. shows the decay curve. The half-life is found to be 2.0 ± 0.1 min.

The beta-decay end point was measured to be 3.3 ± 0.2 MeV with the scintillation spectrometer (Fig. 4). The value is again in good agreement with the beta-decay energy systematics (3.1 MeV).

The gamma-ray spectra of irradiated germanium showed peaks decaying with approximately 2 minutes half-lives. One is at 0.58-MeV having intensity of $\sim 3\%$ of gamma-rays and there may be one at 0.36-MeV with intensity of $\sim 1\%$. The latter is rather weak and does not stand out so clearly in the back ground radiations. Assuming that most of its beta-rays go to the ground state, the log ft value of the beta-decay is 5.2. Since the ground state of Ga^{75} is expected to be $3/2^-$ and the ground state spin of Ge^{75} is $1/2^-$ an allowed transition is expected. Therefore this log ft value is considered to be a proper value for this decay.

As⁸¹

The case of As^{81} is quite similar to the former two isotopes. 99.99% selenium was bombarded with the 25-MeV bremsstrahlung.

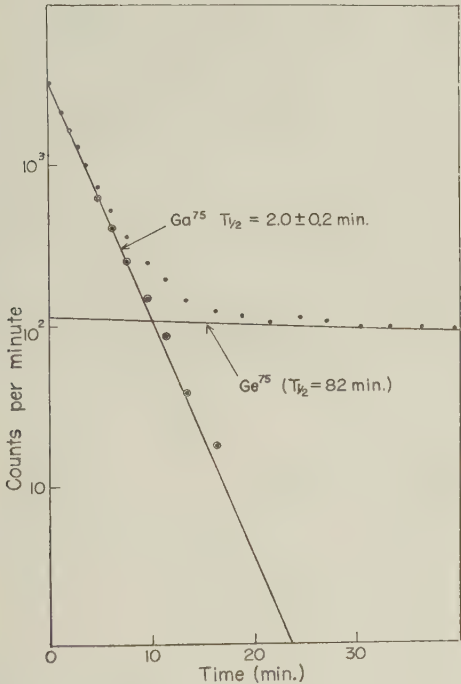


Fig. 3. Decay curve of the high energy beta component of a germanium sample after a bombardment.

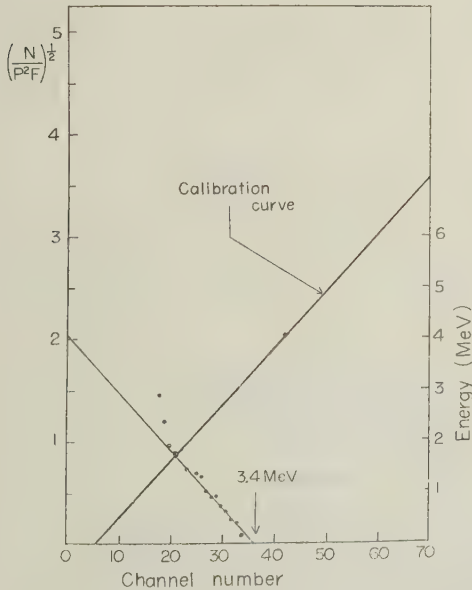


Fig. 4. Kurie plot of beta spectrum of irradiated germanium sample. Self-absorption correction is not applied yet.

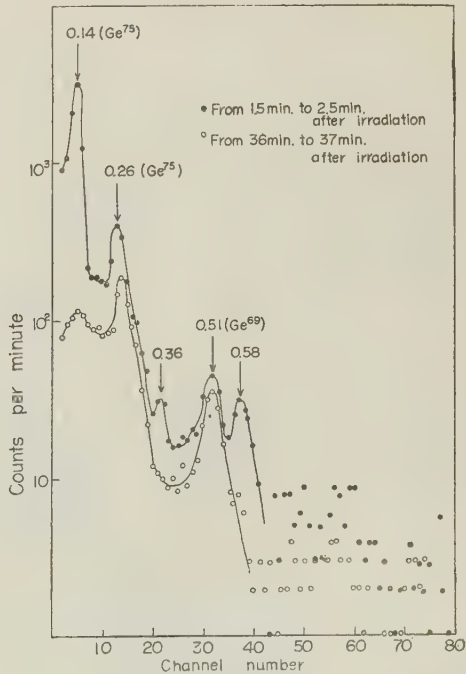


Fig. 5. Gamma-ray spectrum of irradiated germanium sample.

Besides all previously known activities a very short-lived component with approximately 30 sec was observed. In this case, as in the case of Ga^{75} , half-life measured with the G-M counter is disturbed by 3.9 minutes isomer of Se^{79} . Fig. 6 shows the half-life of this short half-lived activity measured by the plastic scintillator discriminated at 2.3-MeV. From this measurement the half-life was determined to be 32 ± 2 sec.

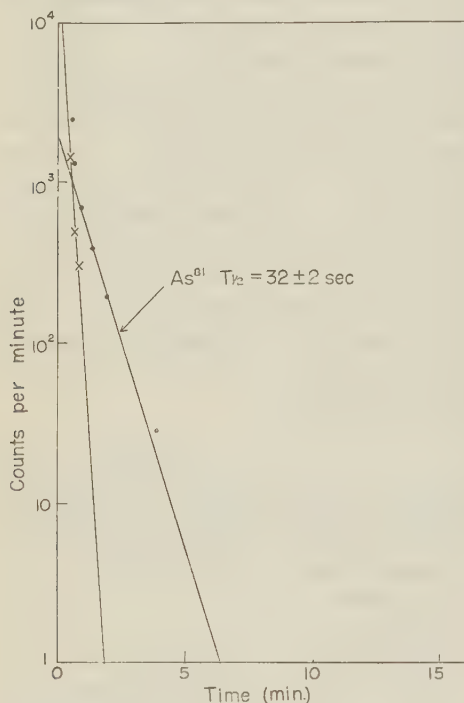


Fig. 6. Decay of high energy beta rays from a irradiated selenium sample. A very short lived component is due to the 6.7 sec Al^{26} produced in the aluminum foil used for wrapping the metallic selenium.

The end point of the beta-decay was found to be 3.8 ± 0.2 -MeV. Fig. 7 shows Kurie plot of beta-spectrum of the activity from 35 sec to 95 sec and from 6 min to 11 min after termination of a bombardment. The 2.2-MeV component is due to As^{79} and 1.5-MeV component is due to Se^{81} . The beta-decay systematics predicts the end point of As^{81} to be 3.8-MeV which is in good agreement with the measured end point of this activity (3.8 ± 0.2 MeV). As in the former case this activity is very certainly assigned to As^{81} . Gamma-ray measurements did not prove any gamma-ray with intensity higher than 1%.

Log ft value of the beta-decay is 4.9. Since the ground state spin of As^{81} is probably $3/2^-$ and that of Se^{81} is $1/2^-$, this is a proper value.

In this case chemical separations were performed in order to see if this activity actually follows arsenic. SeO_2 powder was irradiated about one minute and then dissolved into hot 10N HCl with arsenic carrier and the arsenic was extracted by CCl_4 and counted with the plastic scintillator discriminated at 1.6 MeV and 2.3 MeV. When the discrimination level was set at 1.6-MeV the short-lived component was observed before the 9 minutes decay of As^{79} sets in. When the discrimination level was 2.3 MeV only the 30 sec activity was observed. Thus this 30 sec activity with the high energy radiation is assigned to arsenic.

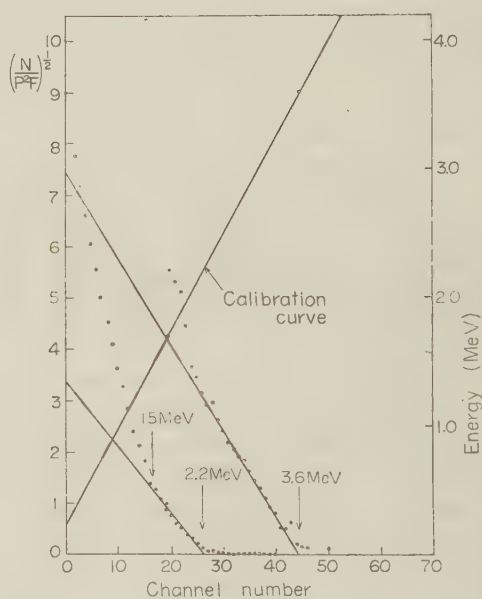


Fig. 7. Kurie plots of irradiated selenium sample. Self-absorption correction is not applied yet.

Cross section ratio of this 30 sec component to the 9 minutes component was almost 1 in this case, too. This shows that even at this low Z the direct process is dominant process since the statistical theory requires much smaller cross sections for heavier isotopes. Again, the value is one of the support of the assignment of this activity to As^{81} . The yield ratio of the (γ, p) to the (γ, n) reaction on Se^{82} is about 1:30 calculating from the beta-ray spectra in Fig. 6.

Acknowledgement

During this investigation we were helped substantially by the members of our nuclear spectroscopy group. The germanium sample was kindly supplied by Miss L. Roth. We are indebted to Dr. N. Suzuki for suggesting us the chemical procedures. Finally we wish to thank Professor M. Kimura for giving us opportunities to use his betatron laboratory.

References

- 1) H. Morinaga and T. Kuroyanagi, to be published in *Nuclear Instruments and Methods*. **5** (1959).
- 2) T. J. Parmley, B. J. Moyer and R. C. Lilly: *Phys. Rev.* **75** (1949) 619.
- 3) K. Way et al: *Nuclear Level Schemes*, U. S. A. E. C. TID-5300 (1955).
- 4) E. D. Courant: *Phys. Rev.* **82** (1951) 703.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

On the Stability of an Electron Gas at Low Density

By Masao SHIMIZU

Department of Physics, Tokyo Metropolitan University

(Received August 1, 1959)

The stability of an electron gas at low density is discussed on the basis of the energy spectrum of a quasi-particle which has been given by the Bohm-Pines theory.

An electron gas at low density has hitherto been considered as to make a lattice in order to save a correlation energy.^{1), 2)} We discuss the stability of the electron gas from a different point of view. If the energy spectrum $\mathcal{E}(k)$ of a quasi-particle having wave vector k (or one-electron energy) in the electron gas is known, the state density $\rho(\mathcal{E})$ is given by

$$\rho(\mathcal{E}) = \frac{V}{2\pi^2} \frac{k^2}{d\mathcal{E}/dk}, \quad (1)$$

where V is the volume of the electron gas. As we do not take the periodic lattice field into account, it will be sure that $\mathcal{E}(k)$ is a function of the magnitude of wave vector k .

According to the Bohm-Pines theory, the energy spectrum of an electron gas having an effective mass m^* in the neighbourhood of the Fermi surface is given by^{3), 4)}

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m^*} - \frac{e^2 k_0}{2\pi} \left\{ 1 + \frac{k_0^2 - k^2}{kk_0} \log \left(\frac{k+k_0}{\beta k_0} \right) + \frac{3k^2 - k_0^2}{2kk_0} - 2\beta + \frac{\beta^2 k_0}{2k} \right\} + \mathcal{E}_{s,r}(k), \quad (2)$$

where the electron gas is considered to be completely degenerate, and $\mathcal{E}_{s,r}(k)$ is the term coming from the second-order perturbation of the screened Coulomb interaction and has

been given explicitly by Fletcher and Larson⁴⁾, and

$$\mathcal{E}_{s,r}(k) = \mathcal{E}_{s,r}^a(k) + \mathcal{E}_{s,r}^p(k). \quad (3)$$

If r_s , the radius of the sphere in the atomic unit whose volume is equal to the volume per electron, is larger than 2, the term, $\mathcal{E}_{s,r}^p(k)$, due to the short-range correlation between electrons with parallel spins may be ignored⁴⁾ and only the term, $\mathcal{E}_{s,r}^a(k)$, due to the short-range correlation between electrons with anti-parallel spins remains in $\mathcal{E}_{s,r}(k)$. When $r_s < 2$, we can use the approximation, $\mathcal{E}_{s,r}^p(k) \approx \mathcal{E}_{s,r}^a(k)$ ⁴⁾. β is given by⁵⁾

$$\beta = k_0/k_0 = 0.47r_s^{1/2}, \quad (4)$$

where k_0 is the maximum plasma oscillation wave vector and k_0 is the magnitude of the wave vector at the Fermi surface. From (2), the value of $d\mathcal{E}/dk$ on the Fermi surface is given by

$$(d\mathcal{E}/dk)_{k=k_0} = (\hbar k_0/m^*) C_1, \quad (5)$$

$$C_1 = 1 + \lambda \left(\log \frac{2}{\beta} - 1 + \frac{\beta^2}{4} \right) + \frac{m^*}{\hbar^2 k_0} \left(\frac{d\mathcal{E}_{s,r}}{dk} \right)_{k=k_0}, \quad (6)$$

where

$$\lambda = \frac{e^2 m^*}{\pi \hbar^2 k_0} = 0.1659(m^*/m)r_s. \quad (7)$$

From Fletcher and Larson's calculation⁴⁾ for the larger r_s , $(d\varepsilon_{s,r.}/dk)_{k=k_0}$ is given in Rydberg unit by

$$\begin{aligned} \pi^2 \frac{d\varepsilon_{s,r.}}{d(k/k_0)} = & \frac{5}{3} \log 2 - 2 - \frac{4}{3} \log \beta \\ & - \frac{4}{3\beta^2} - \frac{4}{3} \frac{\log 2}{\beta^2} \\ & + \left(\frac{\beta}{12} + \frac{2}{3} + \frac{3}{2\beta} + \frac{2}{3\beta^2} - \frac{2}{3\beta^3} \right) \log(2+\beta) \\ & + \left(-\frac{\beta}{12} + \frac{2}{3} - \frac{3}{2\beta} + \frac{2}{3\beta^2} + \frac{2}{3\beta^3} \right) \log(2-\beta). \end{aligned} \quad (8)$$

The relations between r_s and m^*/m which satisfy $C_1=0$ are shown by curve (1) in the case of the approximation, $\varepsilon_{s,r.}(k) \approx 0$, and by curve (2) in the case of the approximation, $\varepsilon_{s,r.}(k) \approx \varepsilon_{s,r.}^a(k)$, in Fig. 1. On this curve, $C_1=0$, that is, $(d\varepsilon/dk)_{k=k_0}=0$. In the upper regions of this curve, $C_1 < 0$, namely $(d\varepsilon/dk)_{k=k_0}$

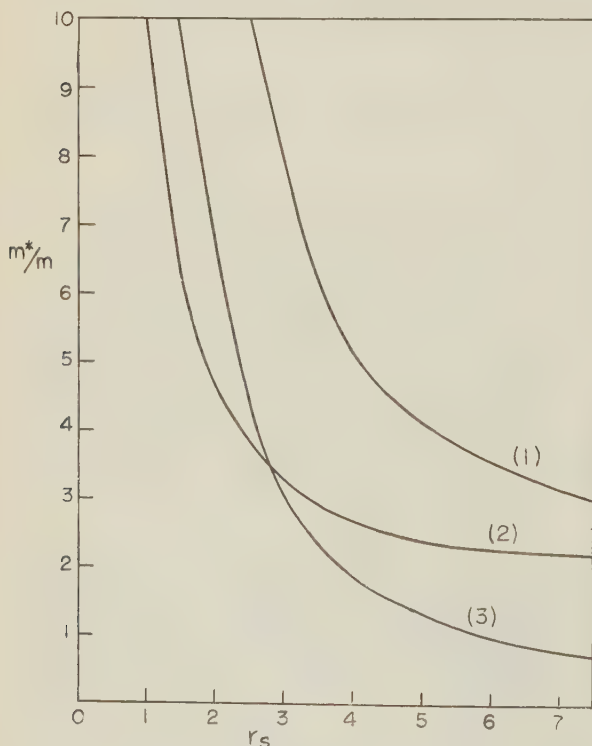


Fig. 1. The relations between r_s and m^*/m which show the limits of the stable configuration of an electron aggregate as a gas are given by curves (1) and (2) obtained from Bohm-Pines' model and by curve (3) obtained from Gell-Mann's calculation on the specific heat of an electron gas respectively.

< 0 . This means that the one-particle energy as a function of the wave vector k has a negative tangent at the Fermi surface, and the relation between $\varepsilon(k)$ and k is schematically shown in Fig. 2. We can easily see that in the case where $(d\varepsilon/dk)_{k=k_0} < 0$ if an electron with the wave vector below k_0 is replaced in the state with the wave vector above k_0 , the energy of the electron gas becomes lower. This fact is not consistent with the assumption at the beginning that the energy of the electron gas which is completely degenerate and in which the states up to k_0 are compactly and doubly occupied by electrons is the lowest at $T=0^\circ\text{K}$. Then we imagine that in the upper region of the curve $C_1=0$, that is, $(d\varepsilon/dk)_{k=k_0} < 0$, the electron gas is unstable and another configuration of electrons such as an electron lattice will be stable. This fact was already pointed out qualitatively by Wigner¹⁾.

Gell-Mann⁵⁾ calculated the specific heat of a degenerate electron gas at high density and obtained the results,

$$C/C_0 = [1 + 0.083r_s(-\log r_s - 0.203)]^{-1}, \quad (9)$$

where C_0 is the specific heat of a free electron gas. If the electron gas has an effective mass m^* , the formula (9) is rewritten as

$$\begin{aligned} C/C_0 &= \left[1 + \frac{m^*}{m} 0.083r_s(-\log r_s - 0.203) \right]^{-1}. \end{aligned} \quad (10)$$

The region of the values of r_s and m^*/m where C becomes negative, that is,

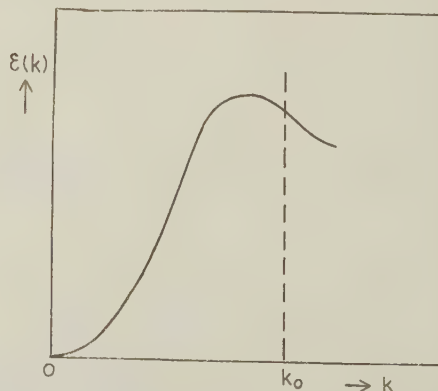


Fig. 2. A qualitative curve of $\varepsilon(k)$ vs. k is shown in the case where the electron gas is unstable.

$$1 + \frac{m^*}{m} 0.083 r_s (-\log r_s - 0.203) < 0, \quad (11)$$

is given by the upper part of curve (3) in Fig. 1. Curve (3) shows the relation

$$1 + \frac{m^*}{m} 0.083 r_s (-\log r_s - 0.203) = 0. \quad (12)$$

Considering that the specific heat of a degenerate electron gas is given by

$$C = \frac{2\pi^2 \kappa^2 T}{3N} \rho(\zeta_0) = \frac{\pi^2 \kappa^2 T}{k_0 (d\varepsilon/dk)_{k=k_0}}, \quad (13)$$

where $\zeta_0 = \varepsilon(k_0)$, the fact that the specific heat is negative, $C < 0$, seems to be caused by the condition $\rho(\zeta_0) < 0$, or $(d\varepsilon/dk)_{k=k_0} < 0$. Then, from the same argument given above, curve (3) in Fig. 1 is considered to represent the limit of the stable treatment of an electron aggregate as a gas. As seen from curve (3) in Fig. 1, when $m^*/m=1$ and $r_s > 6$, the electron gas is not stable as the specific heat becomes negative. However, as Gell-Mann's calculation of the specific heat of an electron

gas is a result which is exactly correct at high density, the use of his result at comparatively low density may not be proper, but the qualitative nature of our discussion in this paper will not be changed after the proper calculation of the state density or the specific heat of an electron gas at low density has been made.

References

- 1) E. P. Wigner: Trans. Farady Soc. **34** (1938) 678.
- 2) J. S. Plaskett: Phil. Mag. **45** (1954) 1255. C. B. Clark: Phys. Rev. **109** (1958) 1133.
- 3) D. Bohm and D. Pines: Phys. Rev. **82** (1951) 625; **85** (1952) 338; **92** (1953) 609; D. Pines: Phys. Rev. **92** (1953) 626; *Solid State Physics* Vol. I (1955) 367.
- 4) J. G. Fletcher and D. C. Larson: Phys. Rev. **111** (1958) 455.
- 5) R. A. Ferrell: Phys. Rev. **107** (1957) 450; K. Sawada, K. A. Brueckner, N. Fukuda and R. Brout: Phys. Rev. **108** (1957) 507.
- 6) M. Gell-Mann: Phys. Rev. **106** (1957) 369.

Detection and Determination of Equilibrium Vacancy Concentrations in Aluminum*

By Soji NENNO** and J. W. KAUFFMAN

*Department of Materials Science, Northwestern University,
Evanston, Ill., U.S.A.*

(Received October 30, 1959)

In order to obtain a direct information concerning the equilibrium vacancy concentrations and the energy of formation of a vacancy in Al, a method of combining the bulk and lattice thermal expansion measurements was used. In the present work, only the lattice thermal expansion measurements on 99.996% pure Al were made. The data obtained were analyzed using bulk thermal expansion data on Al of the same purity available in the literature. The concentration of vacancies increases exponentially with temperature and its value at the melting point is $(1.1 \pm 0.2) \times 10^{-3}$ and the energy of formation of a vacancy is estimated to be $(0.64 \pm 0.12)eV$.

§ 1. Introduction

Atomic imperfections, to which class of defects the vacancy belongs, are characterized by the fact that they can exist in thermodynamic equilibrium in a crystal at finite temperature. The fractional concentration $C (=n/N)$ of vacancies in a monatomic crystal in equilibrium is given by¹⁾

$$C = n/N = \exp(s_v/k) \cdot \exp(-h_v/kT) \quad (1)$$

where s_v and h_v are the additional entropy and energy of formation of a vacancy, respectively, n is the number of vacancies and N is the number of lattice sites, while k and T are the Boltzmann constant and absolute temperature, respectively.

Attempting to estimate the concentration of vacancies and the energy of formation of a vacancy in metals, a number of experimental works have been made using various indirect methods. MacDonald²⁾, in his electrical resistivity measurements on the alkali metals, found an anomalous increase in the resistivity near the melting point and attributed this additional resistivity to the formation of vacancies at the higher temperatures. Meechan and Eggleston³⁾, with a similar type of experiments on Cu and Au, estimated that the concentration of vacancies in Cu near the melting point was of the order of one atomic per cent. Heat capacity

measurements on Al (99.9%) and Pb by Pochapsky⁴⁾ showed that the heat capacity increased very rapidly as the melting point was approached. His estimation of the concentration of vacancies at the melting point was 2×10^{-3} . Jongenburger⁵⁾, using the bulk thermal expansion coefficient data on Au and Cu obtained by Nix and MacNair⁶⁾, estimated the concentration of vacancies and the formation energy from the difference between actual values of the thermal expansion coefficients and those corresponding to a linear extrapolation of Nix and MacNair's expansion coefficient data below about 500°C. He estimated the concentration of vacancies in Au as 5×10^{-4} at 727°C (3×10^{-3} at the melting point of Au) and that in Cu as 3×10^{-4} at 727°C (2×10^{-3} at the melting point of Cu). Gertsriken⁷⁾, also using the thermal expansion data available in the literature, calculated the formation energies and concentrations of vacancies for various metals and alloys with a method somewhat similar to that of Meechan and Eggleston³⁾; for example, in the case of Al (99.9%) the concentration of vacancies at the melting point was about 2×10^{-3} and the formation energy was 0.5 eV. Bradshaw and Pearson⁸⁾ performed a quenching experiment on Au and Al (99.99%) and they found that the concentration of vacancies at the melting point in Al was 6×10^{-4} and the formation energy was 0.76 eV. Turnbull and DeSorbo⁹⁾ found the formation energy of a vacancy in zone purified Al to be 0.79 eV by their quenching experiment. The most recent

* This work was partially supported by the United States Office of Naval Research.

** Now at Department of Metallurgy, Faculty of Engineering, Osaka University.

quenching experiments in Au by Bauerle *et al.*¹⁰⁾ give 7×10^{-4} as the vacancy concentration at the melting point. Although it is thought that the quenching experiment is, in principle, a most accurate method among indirect methods, there are several indeterminate factors present in obtaining this value, for example, a theoretical value is used to convert from quenched-in resistivity to the vacancy concentration. Also, at the present time there is little evidence to indicate what percentage of the vacancies present in equilibrium at the temperature where the quench is begun will anneal out during the quench. The only study of quenching rate is that by Meshii and Kauffman¹¹⁾ on its effect upon the increase in yield stress. They find no leveling off of this effect with increasing quenching speed.

The most direct method for finding the equilibrium concentration of vacancies at higher temperatures is a combination of two kinds of measurements, namely those of the bulk thermal expansion and lattice thermal expansion. Consider a perfect crystal of total volume V_0 with atomic volume v_0 and N_0 lattice points existing in equilibrium at a temperature. After introducing n vacancies, let V be the total volume, v the atomic volume and N the number of lattice points, assuming that we can take an averaged atomic volume throughout the defect crystal. According to Huntington and Seitz¹²⁾ and Dienes¹³⁾ the relaxation of atoms about a vacancy is small in the common metals. Hence, this assumption may be quite reasonable. Thus we have:

$$V_0 = N_0 v_0 \quad (2)$$

$$V = Nv = (N_0 + n)v \quad (3)$$

or rewriting,

$$n = V/v - N_0 = V/v - V_0/v_0.$$

However, since the fractional concentration of vacancies $C = n/N$, we have:

$$C = \frac{V/v - V_0/v_0}{V/v} = \frac{(V/V_0) - (v/v_0)}{V/V_0} \quad (4)$$

where (v/v_0) is measured by X-ray and (V/V_0) by bulk measurement. For cubic isotropic crystals, if l is the length of a sample and a the lattice parameter at a temperature T while l_0 and a_0 are corresponding values at a standard temperature T_0 , the fractional concentration of vacancies, C , present at temperature T is expressed as

$$C \approx 3 \frac{(l/l_0) - (a/a_0)}{(l/l_0)} \quad (5)$$

provided that T_0 is a low enough temperature that $C(T_0)$ is negligible. The objective of the present work is to obtain an information about concentration of vacancies in equilibrium and the energy of formation of a vacancy in pure metal by means of a direct method which consists of bulk thermal expansion and lattice thermal expansion measurements. For the present purpose Al was chosen because it is a face-centered cubic metal of relatively low melting point. During the present work being in progress similar works on Pb by Van Duijn and Van Galen¹⁴⁾ and on Pb and Al by Feder and Nowick¹⁵⁾ have been published. The former did not find any vacancy effect, but the precision attained was not comparable to that of the present measurements. The latter found some evidence of the presence of vacancies in 99.99% pure Al close to the melting point and estimated the concentration of vacancies was 3×10^{-4} . However, since they carried out the bulk and lattice expansion measurements in air, their results seem to appear open to question.

§ 2. Experimental Procedure

A commercial 19 centimeter high temperature powder camera made by Unicam Instruments Ltd., Cambridge, England, (1946 model) was used for measuring lattice thermal expansion. The original platinum-platinum rhodium thermocouple and compensating wires in this instrument were replaced by two calibrated alumel-chromel thermocouples of 13 mils in diameter all the way to the ice cold junctions. As a radiation shield, aluminum foil was pressed against the inner wall at the window by means of stainless steel bands. The camera was constantly evacuated to between 2×10^{-5} and 5×10^{-5} mmHg. The temperature was automatically controlled within $\pm 0.5^\circ\text{C}$ over long periods of time.

The diffraction patterns were measured by a device similar to the one described by Klug¹⁶⁾ which could be read to ± 0.01 mm. In order to obtain the lattice parameter from film measurement, we used a usual method¹⁷⁾, which consists of plotting a graphical extrapolation of spacings *versus* $\frac{1}{2}(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ where θ is Bragg angle. The camera

constants were determined by direct measurements.

According to the works of Berry, Henry and Raynor¹⁸⁾, and of Pease¹⁹⁾ with the same type of camera, the temperature distribution in the gap between the two furnace halves is not uniform, and it is impractical to have direct contact between the thermocouples and specimen. For this reason pure noble metals such as Au or Pt whose thermal expansion is accurately known up to about 1000°C are useful as a temperature standard. Since the melting point is much higher than 1000°C, there is no appreciable concentration of vacancies at the temperature concerned. Consequently, if precision lattice parameters of the standard metal are known at some undetermined temperature and at a standard temperature, say 0°C, we are able to determine the temperature quite satisfactorily by referring back to known thermal expansion data. The lattice parameter of Au near 600°C is almost the same as that of Al. In view of the importance of data close to the melting point of Al, Pt is preferable to Au, provided Co radiation is used which gives Pt a very high Bragg angle θ . Also preliminary experiments showed that the thermal expansion data of Al using Pt as a temperature standard were in good agreement with those using Au. Therefore, it was decided to use Pt as the temperature standard along with Co radiation.

The specimens used were prepared as follows: The materials used were 99.999% pure Pt wires of 3 mils in diameter and 99.996% pure Al rods of $\frac{1}{4}$ inch in diameter, supplied by the Johnson and Mathey Company. Here the Pt wires were annealed at 900°C for an hour in helium. A portion of the Al rod was cold-drawn to 20 mils in diameter, etched with 10% NaOH solution down to about 5 mils in diameter and finally cleaned with distilled water many times. It was then immersed in dilute HCl solution and again washed with distilled water, followed by a dip in ethyl alcohol, a washing with ethyl ether and drying. The wire thus finished was cut into pieces 3mm in length. A few of them were inserted into a thin-walled quartz capillary around which a length of high purity Pt wire was wound. See Fig. 1. A length of quartz rod was then inserted on

top of the Al thin rods. The capillary was fused to the quartz tubing connected to the evacuating system. After the ultimate vacuum was reached (in the order of 10^{-7} mmHg) the specimen was heated by a small furnace to about 650°C and kept there until the vacuum reached a constant value of 2×10^{-7} mmHg. The vacuum was measured by a Miller cold cathode gauge M-40312, manufactured by H. S. Martin and Co., which is sensitive to 0.1×10^{-7} mmHg. Then the capillary was sealed off at a suitable length.

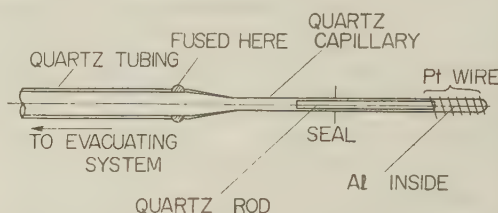


Fig. 1. Schematic diagram of preparing specimen.

With each of the specimens thus prepared, the experiments were made as follows: After a specimen was mounted properly and the thermal equilibrium was reached at room temperature without evacuating the camera, two photographs were taken at this temperature which was measured by the thermocouples. A single photograph gave the reflections from Al and the standard metal simultaneously. The lattice parameters of Al and the standard metal at that temperature were obtained from these photographs. The values of lattice parameter for each metal were averaged. The temperature variation during exposure was within $\pm 0.5^\circ\text{C}$. At room temperature it was assumed that the mean temperature as read by the thermocouples was equal to that of the specimen. This point was examined by moving one of the thermocouples, which was attached to the upper half of the furnace, up and down, while the other was kept in the same position flush with the top surface of the lower half of the furnace. It was found that the temperature difference between two thermocouples was less than 0.5°C . Using Taylor's data²⁰⁾ for the thermal expansion of Al and Esser and Eusterbrock's²¹⁾ for that of the standard metal, the lattice parameters at 0°C of Al and the standard metal were calculated. Then the camera was evacuated and the temperature was gradually raised to desired

temperatures, where exposures were made. At least one exposure was made at each temperature. As the lattice parameter of Al and that of the standard metal can be obtained simultaneously from a single photograph at each temperature, the values of lattice parameter for each metal were averaged when two or more exposures were made. Then the temperature of the specimen was determined from the lattice parameter of the standard metal, dividing it by the lattice parameter, at 0°C, of the standard metal of the same specimen and finding the relative thermal expansion and referring back to Esser and Eusterbrock's data²¹⁾ for the thermal expansion of the standard metal. In this way the lattice parameters of Al at various temperatures and the relative thermal expansion data relative to 0°C were obtained. After having taken photographs at high temperatures, the specimen was occasionally cooled down to room temperature and exposures were made to check if there was any contamination of the specimen. The probable errors involved in determining lattice parameter at about 650°C and temperature of the specimen were found to be as follows: Probable error in lattice parameter of Pt is 1.5×10^{-5} and hence probable error in temperature measurement is 1.5°C; probable error in lattice parameter of Al is 5×10^{-5} .

Since the Pt wire used as a thermometer and the thin rods of Al are not in direct contact with each other but separated by a thin quartz wall, it is necessary to test whether or not there is any temperature difference between them. For this purpose two different methods were used.

In the first method, the Al thin rods were replaced by Au whose thermal expansion is accurately known. 99.999% pure Au thin rods were used along with the thermal expansion data obtained by Esser and Eusterbrock²¹⁾. The specimen was prepared using the previously mentioned procedure. Since a single film gives the reflections from Pt and Au simultaneously, from the lattice parameter of each metal measured we can find the temperature of Au and that of Pt, respectively. Two photographs at room temperature and two photographs at about 665°C were taken. After cooling the specimen back to room temperature, another two photo-

graphs were taken. From the lattice parameters obtained from these photographs the temperature as given by Pt and that by Au were calculated by making use of the known thermal expansion data for the two metals. The temperature derived from the thermal expansion of Pt (665°C) agreed with that derived from the thermal expansion of Au (664°C) with a discrepancy of 1°C. The second method involved disappearance of reflection lines from Al at its melting point. As described in Wilson's paper²²⁾, a number of exposures were made near the melting point of Al, and the melting point was determined by disappearance of the reflection lines. The average value of the melting point as determined in this way is found to be 661°C, while the value of the melting point given in ASM Metals Handbook²³⁾ is $(660.2 \pm 0.1)^\circ\text{C}$. Since the probable error involved in temperature determination by means of the thermal expansion of Pt was $\pm 1.5^\circ\text{C}$, it is concluded that there is no appreciable temperature difference between the outside and inside of the quartz capillary.

§ 3. Results

The results are given in Fig. 2 plotting a/a_0 against temperature, where a and a_0

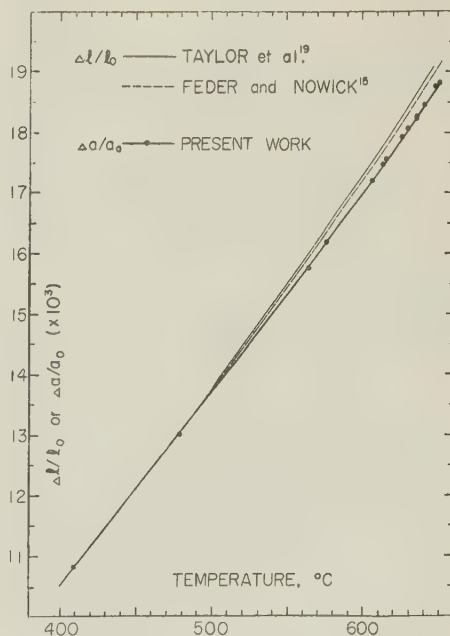


Fig. 2. Comparison of lattice⁹ and bulk thermal expansion of Al, where $\Delta l/l_0 = (l - l_0)/l_0$ and $\Delta a/a_0 = (a - a_0)/a_0$.

denote the lattice parameter of Al at a temperature concerned and that at 0°C, respectively. The lattice parameter of Al as measured at 25°C is 4.0496₂ Å. Using Taylor's²⁰⁾ empirical equation, the lattice parameter at 0°C is calculated to be 4.0472₆ Å. The numerical values of the lattice thermal expansion as obtained from the present experiments are given in Table I. The wave lengths used

Table I. Lattice thermal expansion of Al as obtained in the present work.

Temperature °C	<i>a</i> Å	<i>a/a</i> ₀
25	4.0496 ₂	(1.00058)*
96	4.0562 ₄	1.00222
208	4.0680 ₂	1.00513
298	4.0778 ₈	1.00757
383	4.0876 ₆	1.00998
409	4.0909 ₆	1.01080
479	4.0999 ₁	1.01301
564	4.1110 ₂	1.01575
575	4.1127 ₄	1.01618
605	4.1168 ₉	1.01720
612	4.1179 ₇	1.01747
615	4.1182 ₉	1.01755
626	4.1197 ₉	1.01792
630	4.1203 ₉	1.01807
635	4.1210 ₈	1.01824
636	4.1209 ₂	1.01820
641	4.1218 ₇	1.01844
648	4.1231 ₁	1.01874
649	4.1232 ₉	1.01878
651	4.1234 ₃	1.01882

* Calculated using Taylor's empirical equation²⁰⁾.

Table II. Comparison of lattice thermal expansion.

Author	<i>(a - a</i> ₀ <i>)/a</i> ₀ × 10 ³ at					
	200°C	300°C	400°C	550°C	600°C	650°C
Feder and Nowick ¹⁶⁾	4.85*	7.65*	10.60*	15.40*	17.15	19.00*
Wilson ²²⁾	4.82	7.57	10.52	—	17.21	19.07
Present work	4.89	7.61	10.53	15.31	17.02	18.80

* These values are obtained from their graph.

are 1.78890 Å for Co *K*α₁, and 1.79279 Å for Co *K*α₂. From the *a/a*₀ values given in Table I an empirical equation for the lattice thermal expansion of Al was worked out by the method of least square. It is given as

$$a/a_0=1+2.2724t\times10^{-5}+8.188t^2\times10^{-9}+2.02t^3\times10^{-12}, \tag{6}$$

where *t* is temperature in °C, and *a*₀ and *a*

are the lattice parameters at 0° and *t*°C, respectively, the maximum deviation being 0.08 × 10⁻³ and the average deviation 0.03 × 10⁻³. A comparison was made between our data and those published by previous investigators¹⁶⁾²²⁾, who used Al of comparable purity (99.99%), as given in Table II. It is noted from Table II that they are in good agreement with each other up to about 400°C and are in fair agreement at higher temperatures, i.e., our values are lower than the others at temperatures above about 500°C, for instance, by 0.20 × 10⁻³ to 0.27 × 10⁻³ at 650°C. In an attempt to know where this slight discrepancy came from, the following experiments were performed:

(1) A specimen was prepared as described in the earlier section except that a little hole at the top of the capillary was made in order to allow air to enter freely into the capillary. After taking a photograph at room temperature, the camera was operated at low vacuum. A photograph was taken at 640°C at a pressure of 25 to 40 microns Hg with 26 hours exposure. The lattice parameters are: *a* = 4.1229₂ Å at 640°C, *a*₀ = 4.0472₆ Å at 0°C, and *a/a*₀ = 1.01869. This *a/a*₀ value is larger by 0.26 × 10⁻³ than the value *a/a*₀ = 1.01843 calculated from the empirical equation (6).

(2) Since the present camera was not suitable for operating in open air, an alternative method was adopted. Al thin rods of about 3mm length, prepared just as described in the earlier section, were annealed at 650°C for 13 hours in a quartz tube whose one end is open to the air. A portion of the Al thin rods annealed in air was inserted into a quartz capillary, and the capillary was sealed off under ordinary atmospheric pressure instead of high vacuum. The camera was operated in a normal condition. At room temperature two photographs were taken before heating up the specimen. Three photographs were taken at 637°C and one photograph was taken after cooling the specimen. The averaged values of lattice parameters at 0° and 637°C, as compared with those calculated from the empirical equation (6) using *a*₀ = 4.0472₆ Å, are:

	in air	in vacuum
637°C	<i>a</i> = 4.1226 ₃ Å	4.1213 ₇ Å (calculated)
0°C	<i>a</i> ₀ = 4.0473 ₅ Å	4.0472 ₆ Å (calculated)
	<i>a/a</i> ₀ = 1.01860	1.01831

The *a/a*₀ value (air) at the left column is larger

by 0.29×10^{-3} than the a/a_0 value (vac.) at the right column. Therefore, these observations suggest that the slight discrepancy between the results of the previous investigations and those of the present work may be explained in terms of the difference in the degree of vacuum used.

According to equation (1) and (5), we can obtain values of the energy of formation of vacancy and equilibrium vacancy concentrations in Al, provided that bulk thermal expansion data on Al of the same purity are available. In the literature there are three independent data available, namely, of Taylor *et al.*²⁰⁾, Feder and Nowick¹⁵⁾, and Nix and MacNair⁶⁾ with 99.996, 99.997, and 99.997% pure Al, respectively. The highest temperature reached in Nix and MacNair's interferometric measurements is about 400°C. Up to this temperature the results obtained by three independent investigators are in good agreement with each other. Taylor *et al.* carried out their interferometric measurements up to 500°C and gave an empirical equation:

$$l_t/l_0 = 1 + (23.22t + 0.00467t^2 + 0.0000078t^3) \cdot 10^{-6} \quad (7)$$

where l_t and l_0 are the lengths at t° and 0°C , respectively. Using equation (7) we calculated numerical values of bulk thermal expansion at some selected temperatures. The values of equilibrium concentration of vacancies can be obtained at various temperatures using equation (5). The results of these calculations are listed in Table III. A plot

Table III. Vacancy concentrations at various temperatures, with use of Taylor's bulk thermal expansion data.

$t^\circ\text{C}$	$1/T \times 10^3$	l/l_0	a/a_0	$C \times 10^3$
550	1.215	1.01547	1.01531	0.48
575	1.179	1.01638	1.01616	0.66
600	1.145	1.01730	1.01702	0.84
625	1.114	1.01825	1.01789	1.05
650	1.083	1.01921	1.01879	1.23
660*	1.072*	1.01960*	1.01915*	1.32*

* extrapolated.

of $\log C$ against the reciprocal of absolute temperature is given in Fig. 3, which shows a linear relationship. Hence, the values of the energy of formation of a vacancy, h_v , and additional entropy associated, s_v , in equation (1) can be obtained. The values of the

quantities, C at the melting point, h_v , and s_v/k as obtained from Fig. 3 are: $C(\text{m.p.}) = (1.3 \pm 0.1) \times 10^{-3}$, $h_v = (0.61 \pm 0.07)eV$, and $s_v/k = 0.31$ to 1.0. Feder and Nowick made bulk thermal expansion measurements up to the melting point of Al. Using their data¹⁵⁾, we can obtain the corresponding quantities in the same way as in the former case. The results are given in Table IV and are presented in Fig. 3 as a plot of $\log C$ against $1/T$ which shows approximately a linear relationship. The values of C at the melting point, h_v , and s_v/k as estimated from Fig. 3 are:

Table IV. Vacancy concentrations at various temperatures, with use of Feder and Nowick's bulk thermal expansion data.

$t^\circ\text{C}$	$1/T \times 10^3$	l/l_0	a/a_0	$C \times 10^3$
550	1.215	1.01542	1.01531	0.33
575	1.179	1.01632	1.01616	0.48
600	1.145	1.01720	1.01702	0.54
625	1.114	1.01815	1.01789	0.75
650	1.083	1.01910	1.01879	0.93
670*	1.072*	1.01949*	1.01915*	1.02*

* extrapolated.

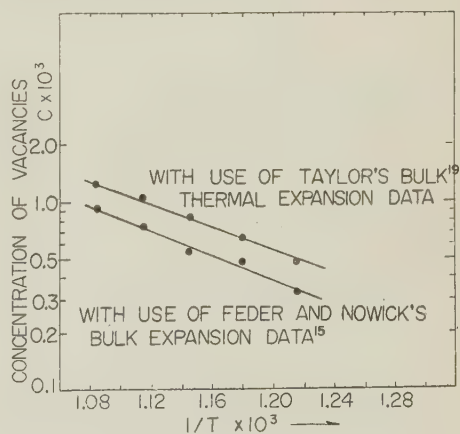


Fig. 3. Plots of concentration of vacancies against reciprocal of absolute temperature.

$C(\text{m.p.}) = (1.0 \pm 0.1) \times 10^{-3}$, $h_v = (0.67 \pm 0.09)eV$, and $s_v/k = 0.6$ to 2.5. The two sets of these values obtained from two independent data of the bulk thermal expansion are not greatly different. Upon averaging them we have: $C(\text{m.p.}) = (1.1 \pm 0.2) \times 10^{-3}$, $h_v = (0.64 \pm 0.12)eV$, and $s_v = 1.4$ (ranging between 0.3 and 2.5).

§ 4. Discussion

The results of the present work are com-

pared with those obtained by the various indirect methods as follows: Meechan and Eggleston's estimation³⁾, $C(\text{m.p.}) \cong 10^{-2}$ for Au and Cu, may be too high. Pochapsky's⁴⁾ $C(\text{m.p.}) = 2 \times 10^{-3}$ for Al, Jongenburger's⁵⁾ $C(\text{m.p.}) = 3.3 \times 10^{-3}$ for Au, 2.0×10^{-3} for Cu, and Gertsriken's⁷⁾ $C(\text{m.p.}) = 2 \times 10^{-3}$ for Al are of the same order of magnitude as ours, that is $C(\text{m.p.}) = (1.1 \pm 0.2) \times 10^{-3}$, although they seem to be a little too large. Bradshaw and Pearson⁸⁾, from the quenching experiment on 99.99% pure Al, reported that $C(\text{m.p.})$ was 6×10^{-4} using 1.5 micro-ohm-cm per at. % vacancies, $h_v = (0.76 \pm 0.03)eV$. DeSorbo and Turnbull⁹⁾, from a similar experiment on zone refined Al, found h_v to be $(0.79 \pm 0.04)eV$ and estimated $C(\text{m.p.})$ as 10^{-3} using 1.4 micro-ohm-cm per at. % vacancies. The value of $C(\text{m.p.})$ obtained from the quenching experiment on Au by Bauerle *et al.*¹⁰⁾ is 7×10^{-4} , which is in good agreement with that found in Al. These results obtained from the quenching experiments are in fairly good agreement with our results.

Concerning a more direct method, Feder and Nowick¹⁵⁾, who carried out bulk and lattice thermal expansion measurements on Al and Pb, obtained $C(\text{m.p.})$ in Al of 3×10^{-4} . They were not able to determine h_v experimentally because the difference of bulk and lattice thermal expansion at higher temperature was too small to find out an exponential dependence of C upon temperature. Comparing their value of $C(\text{m.p.})$ with that of the present work it is less than one third of our result. It is evident that this discrepancy is due to a difference in the lattice thermal expansion data. It is suggested that this discrepancy in the lattice thermal expansion data may be due to the fact that they made their measurements in air. As found in the present work the lattice thermal expansion a/a_0 of Al annealed in air at 637°C is higher than that of Al annealed under high vacuum by an amount of 0.29×10^{-3} in a/a_0 . This approximately corresponds to the discrepancy between a/a_0 values of the two investigations. This paper is based on a thesis submitted by S. Nenno to the Faculty of the Graduate School of Northwestern University as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Note Added in Proof.

Very recently it came to our notice that Simmons and Balluffi²⁴⁾ carried out the bulk and lattice thermal expansion measurements on Al of 99.995% purity to determine equilibrium vacancy concentrations. Their values of $C(\text{m.p.})$ and h_v are 9.4×10^{-4} and $0.76eV$, respectively. These results agree with ours.

References

- 1) H. Brooks' article in *Impurities and Imperfections* (Amer. Soc. Met., Cleveland, 1955).
- 2) D. K. C. MacDonald: *J. Chem. Phys.* **21** (1953) 177.
- 3) C. J. Meechan and R. R. Eggleston: *Acta Met.* **2** (1954) 680.
- 4) T. E. Pochapsky: *Acta Met.* **1** (1953) 747.
- 5) P. Jongenburger: *Phys. Rev.* **106** (1957) 66.
- 6) F. C. Nix and D. MacNair: *Phys. Rev.* **60** (1941) 597; *Phys. Rev.* **61** (1942) 74.
- 7) S. D. Gertsriken: *Physics of Metallurgy and Metallography* **3** (1956) 238.
- 8) F. J. Bradshaw and S. Pearson: *Phil. Mag.* **2** (1957) 379, 570.
- 9) W. DeSorbo and D. Turnbull: *Acta Met.* **7** (1959) 83; Private communication.
- 10) J. E. Bauerle and J. S. Koehler: *Phys. Rev.* **107** (1957) 1493. F. Seitz, J. S. Koehler and J. E. Bauerle: *ibid.*, 1499.
- 11) M. Meshii and J. W. Kauffman: *Acta Met.* **7** (1959) 180.
- 12) H. B. Huntington and F. Seitz: *Phys. Rev.* **61** (1942) 315.
- 13) G. J. Dienes: *Phys. Rev.* **66** (1952) 228.
- 14) J. Van Duijn and J. Van Galen: *Physica* **23** (1957) 622.
- 15) R. Feder and A. S. Nowick: *Phys. Rev.* **109** (1958) 1959; Private communication.
- 16) H. P. Klug: *Ind. Eng. Chem., Anal. Ed.* **12** (1940) 753.
- 17) A. J. C. Wilson and H. Lipson: *Proc. Phys. Soc.* **53** (1941) 235. J. B. Nelson and D. P. Riley: *Proc. Phys. Soc. London* **57** (1945) 106. I. G. Edmunds, H. Lipson and H. Steeple's article in *X-Ray Diffraction by Polycrystalline Materials* (Inst. Phys., London, 1955).
- 18) B. L. Berry, W. G. Henry and G. V. Raynor: *J. Inst. Metals*, **78** (1951) 643.
- 19) R. S. Pease: *J. Sci. Instr.* **32** (1955) 476.
- 20) C. S. Taylor and *et al.*: *Metals and Alloys* **9** (1938) 189.
- 21) H. Esser and H. Eusterbrock: *Arch. Eisenhuettenw.* **14** (1941) 341.
- 22) A. J. C. Wilson: *Proc. Phys. Soc. London* **54** (1942) 487.
- 23) *Metals Handbook* (American Society for Metals, 1948) p. 20.
- 24) R. O. Simmons and R. W. Balluffi: Private communication.

Une Nouvelle Forme du Nitrure de Nickel: Ni_4N

Par Nobuzo TERA0

*European Research Associates, s. a. 95, rue Gatti de Gamond
Bruxelles 18, Belgique*

(Received November 2, 1959)

The transformation of nickel lattices under the influence of nitrogen as an insertion impurity has been followed by electron diffraction after nitriding thin monocrystalline evaporated films of nickel in an atmosphere of ammoniac at different temperatures.

As established previously, the nitriding process occurs as follows: $\text{Ni}(\text{f.c.c.}, a = 3.52 \text{ \AA}) \rightarrow \text{Ni}_4\text{N}(\text{f. c. c.}, a = 3.72 \text{ \AA}) \rightarrow \text{Ni}_3\text{N}(\text{hexagonal})$.

In this work, a detailed study of some anomalous diffraction spots reported, but not interpreted in a previous work, has been undertaken. It has been found that these anomalous diffraction spots appear rather clearly on the specimens nitrided at $230\text{--}240^\circ\text{C}$ and they belong to a new form of Ni_4N which is no longer cubic but tetragonal. Its lattice parameters are:

$$a=b=3.72 \text{ \AA}; c=2c^*=7.28 \text{ \AA}$$

These interpretations provide evidence of existence of two forms of Ni_4N : one cubic: $\text{Ni}_4\text{N}(\text{I})$ and the other, tetragonal: $\text{Ni}_4\text{N}(\text{II})$. The tetragonal form $\text{Ni}_4\text{N}(\text{II})$ is derived from the cubic form $\text{Ni}_4\text{N}(\text{I})$. This occurs as follows: Two elementary lattices of cubic $\text{Ni}_4\text{N}(\text{I})$ join together after contraction along $[c]$ axis (from $c=3.72 \text{ \AA}$ to $c^*=3.64 \text{ \AA}$) and form a unit cell of the tetragonal form. The two other axes $[a]$ and $[b]$ conserve their initial value of $3.72 \text{ \AA}$ ($c^*/a=0.98$).

§ 1. Introduction

Dans les notes précédentes^{1),2)}, nous avons décrit la transformation du nickel sous l'influence de l'azote. Cette transformation, étudiée par diffraction électronique, se fait suivant le schéma, $\text{Ni}(\text{c.f.c. } a=3.52 \text{ \AA}) \rightarrow \text{Ni}_4\text{N}(\text{cubique, } a=3.72 \text{ \AA}) \rightarrow \text{Ni}_3\text{N}(\text{hex. } a=2.66 \text{ \AA}, c=4.30 \text{ \AA})$.

La maille cubique à faces centrées du nickel se dilate d'abord par l'insertion des atomes d'azote avec, comme conséquence, la formation du nitrure; Ni_4N . La structure de ce nitrure est c. f. c. pour les atomes de nickel avec, en plus, un atome d'azote au centre de la maille élémentaire. Ensuite, si la nitruration est poursuivie, la maille c. f. c. dilatée se transforme en une maille hexagonale compacte correspondant au Ni_3N . Le mécanisme de cette transformation comprend: (a) changement de l'ordre d'empilement des plans $\{111\}$ -cubique en un empilement des plans $\{0001\}$ -hexagonal qui se produit par des microglissements sur les plans $\{111\}$ dans la direction $[11\bar{2}]$ et (b) la diffusion des atomes d'azote dans le réseau du Ni_4N provoquant un autre change-

ment de l'ordre d'empilement: les plans $\{1\bar{1}0\}$ -cubique deviennent, après la transformation, les plans $\{1\bar{2}10\}$ -hexagonal.

Au cours de ces études, nous avons constaté que, pour une couche mince monocrystalline de Ni nitruré à 230°C environ, certaines réflexions anormales apparaissent lors de la transformation $\text{Ni}_4\text{N} \rightarrow \text{Ni}_3\text{N}$. Il s'agit,

(1) d'une tache $(1, \frac{1}{2}, 0)$ et

(2) d'une tache $(1\ 0\ 0)$ qui correspond à une distance réticulaire de $3.63 \text{ \AA}$. Cette valeur est beaucoup plus petite que la valeur $3.72 \text{ \AA}$ obtenue sur le diagramme ordinaire du Ni_4N et cette différence dépasse largement l'erreur expérimentale comme nous le signalons dans notre publication. (Fig. 8 et Tableau III de la Bibliographie (2)). Ces données n'étant pas suffisantes pour comprendre à quoi il faut attribuer cette anomalie, il nous a semblé opportun de chercher d'autres renseignements qui permettent de compléter notre étude sur les nitrures de nickel. C'est pourquoi nous avons repris la nitruration d'une couche mince monocrystalline de nickel obtenu par vaporisation sous vide sur une face clivée

de NaCl chauffé à 400–450°C.

§ 2. Résultats Expérimentaux

La nitruration a été faite comme auparavant par passage de gaz ammoniac sur des couches de nickel chauffées à des températures allant de 180 à 450°C. Après avoir répété cette expérience plusieurs fois, nous avons obtenu de nouveaux résultats au sujet des taches anormales. Ces taches apparaissent par nitruration à 180–250°C mais elles sont normalement très faibles et diffuses car il est difficile d'arrêter exactement la nitruration à ce stade assez fugace.

C'est surtout par nitruration à 230–240°C qu'on obtient un diagramme qui montre assez nettement l'apparition de ces taches. Les diagrammes typiques de diffraction électronique obtenus sur des échantillons nitrurés dans cette région de température sont présentés dans les Fig. 1 et 2 auxquelles correspondent les traitements suivants. Fig. 1: couche vaporisée nitrurée pendant une heure à 230°C, soit sur support de sel-gemme, soit sur support de grille métallique sans membrane de collodion. Fig. 2: couche vaporisée, détachée du support NaCl, déposée sur membrane de collodion et nitrurée 4 heures à 240°C. Il faut remarquer que le degré de nitruration est assez différent pour ces deux traitements. La Fig. 1 montre des taches appartenant à $(\text{Ni} + \text{Ni}_3\text{N})$ et des taches anormales comme dans la Fig. 8 de la Bibliographie (2). Par contre, la Fig. 2 montre des taches de $(\text{Ni} + \text{Ni}_4\text{N})$ ordinaire) et des taches anormales. On remarque dans ces figures trois nouvelles réflexions;

(1) tache $(1, 3/2, 0)$, marquée par le chiffre 1 dans la Fig. 3, correspondant à une distance réticulaire de 2.04 Å.

(2) tache (200) qui correspond à 1.82 Å. Cette valeur est exactement la moitié de la valeur 3.64 Å de la tache $(1\ 0\ 0)$. Cela indique que ces deux taches appartiennent à la même série de réflexions. La tache 1.82 Å est marquée dans la Fig. 3 par le chiffre 2.

(3) tache $(2\ 2\ 0)$, marquée par le chiffre 3, correspondant à une distance réticulaire 1.31 Å.

Les taches (2) et (3) apparaissent respectivement tout près des taches intenses (200) et (220) , c'est pourquoi il est très difficile de les distinguer. De plus, le diagramme anormal

obtenu jusqu'à présent coexiste toujours soit avec le diagramme du Ni_4N normal, soit avec le diagramme du Ni_3N . Dans le premier cas, la tache (100) 3.64 Å de la Fig. 3 est superposée partiellement sur la tache (100) 3.72 Å du Ni_4N . Dans le deuxième cas, la tache (1,

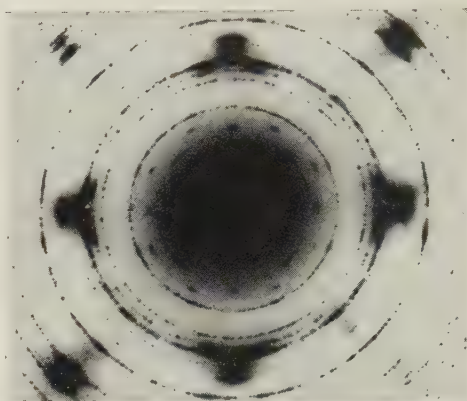


Fig. 1. Diagramme de diffraction électronique de $(\text{Ni} + \text{Ni}_3\text{N} + \text{Ni}_4\text{N}, \text{II})$.

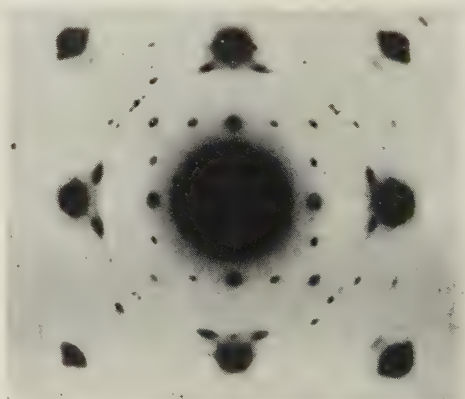


Fig. 2. Diagramme de diffraction électronique de $(\text{Ni} + \text{Ni}_4\text{N}, \text{I} + \text{Ni}_4\text{N}, \text{II})$.

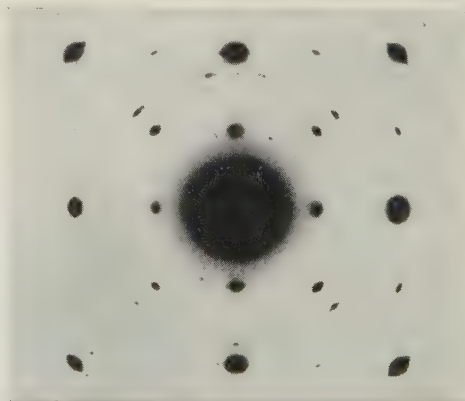


Fig. 7. Diagramme de diffraction électronique de $\text{Ni}_4\text{N}, \text{I}$.

Dans les deux cas, deux mailles cubiques forment une maille élémentaire de la nouvelle forme tétragonale. Le paramètre $a=3.72 \text{ \AA}$ de la forme cubique (Ni_4N) diminue légèrement à $c^*=3.64 \text{ \AA}$ par la formation d'une structure ordonnée dans la direction $[c]$. Les deux autres paramètres de la forme tétragonale a et b conservent toujours la valeur $a=3.72 \text{ \AA}$. Le rapport $c^*/a=0.98$. La structure de la Fig. 6(a) ressemble à la structure Ag_3Mg

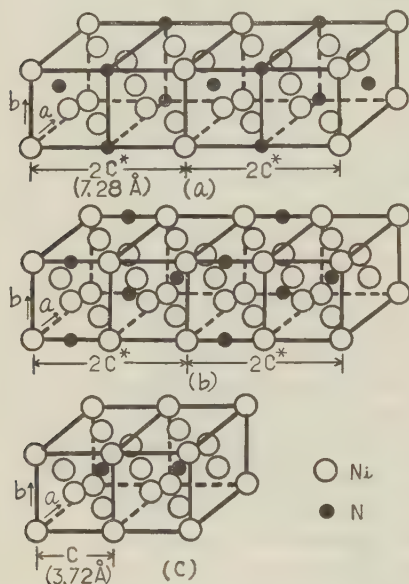


Fig. 6. Trois modèles de la structure du nitrure de nickel. (a) type A_3B , (b) type $\text{A}_4\text{B}(\text{Ni}_4\text{N}, \text{II})$ et (c) $\text{Ni}_4\text{N}, \text{I}$.

ordonné³⁾, structure uni-dimensionnelle d'antiphase, mais avec une valeur $M=1$. Au moyen du seul diagramme de diffraction et sans renseignement quantitatif sur l'intensité de réflexion, on ne peut pas déterminer laquelle des deux formes est présente, car la distribution des taches que donne chacune de ces deux formes est tout-à-fait la même. Cependant, si on considère le fait que le diamètre de l'atome d'azote est beaucoup plus petit que celui de l'atome de nickel, le paramètre $a(=b)$ d'une forme tétragonale devrait être plus petit que le paramètre $a=3.52 \text{ \AA}$ de la maille

c. f. c. de nickel pour le cas de la Fig. 6(a). En réalité, le nitrure observé conserve la valeur $a=3.72 \text{ \AA}$ du Ni_4N . Ce résultat nous fait suggérer que l'apparition de la forme A_3B est moins probable que la forme A_4B . D'autre part, nous avons proposé dans le rapport précédent que les atomes d'azote, situés au centre d'une maille cubique de Ni_4N , diffusent au cours de la transformation $\text{Ni}_4\text{N} \rightarrow \text{Ni}_3\text{N}$ non seulement dans le plan $[\bar{1}10]$, mais aussi dans la direction $[1\bar{1}0]$. La formation du type A_4B de la Fig. 6(b) appuie ce mécanisme de diffusion des atomes d'azote. Cette interprétation nous amène à conclure à l'existence d'une nouvelle forme de Ni_4N . Nous appellerons ce nitrure le $\text{Ni}_4\text{N}, \text{II}$ et le Ni_4N du type Fig. 6(c), trouvé dans le travail antérieur, le $\text{Ni}_4\text{N}, \text{I}$. D'après cette interprétation, la Fig. 1 contient les diagrammes de $(\text{Ni}+\text{Ni}_3\text{N}+\text{Ni}_4\text{N}, \text{II})$ et la Fig. 2 $(\text{Ni}+\text{Ni}_4\text{N}, \text{I}+\text{Ni}_4\text{N}, \text{II})$. Par contre, la Fig. 7 montre le $\text{Ni}_4\text{N}, \text{I}$ seul.

L'apparition de la forme $\text{Ni}_4\text{N}, \text{II}$ a été observée également dans la transformation provoquée par l'action d'un faisceau d'ions oxygène et azote⁴⁾.

Remerciements

Ce travail a été supporté matériellement par l'Union Carbide Corporation, New York et il est très agréable pour l'auteur de lui exprimer sa reconnaissance pour ce soutien. L'auteur remercie également Dr. R. H. Gillette et Dr. A. Berghezan pour leur encouragement constant et l'intérêt qu'ils ont mis dans ce travail.

Bibliographie

- 1) N. Terao: *Naturwiss.* **45** (1958) 620; **46** (1959) 204.
- 2) N. Terao et A. Berghezan: *J. Phys. Soc. Japan* **14** (1959) 139.
- 3) K. Fujiwara, M. Hirabayashi, D. Watanabe and S. Ogawa: *J. Phys. Soc. Japan* **13** (1958) 167.
- 4) J. J. Trillat, L. Tertian et N. Terao: *C.R. Acad. Sci., Paris* **243** (1956) 666.

Crystal Texture of LiF Single Crystals by X-Ray Technique

By Hiroshi NIMURA

*Department of Physics, Tokyo Metropolitan University,
Setagaya-ku, Tokyo, Japan*

(Received October 1, 1959)

By the convergent X-ray beam method with transmission type monochromator by Kato (*Acta Met.* **5** (1957) 237), crystal texture of as-grown LiF single crystals is studied for thick as well as thin specimens. It is found that the topographic as well as the goniometric information is obtainable on a diffraction photograph by the profitable use of the convergent incident beam.

Observation of surface texture is also carried out by etching method to interpret more thoroughly the fine structure of diffraction pattern.

§ 1. Introduction

For the investigation of mosaic misorientations in crystals Kato¹⁾ used the convergent X-ray beam method with a bent monochromator of the transmission type by modifying the reflection type by Lambot *et al.*²⁾ Kato's method has the high angular resolution of the mosaic misorientation and enables the point-to-point correspondence between the specimen and its diffraction pattern to be obtained along the irradiated narrow linear region of the specimen. He applied this method both to the transmission arrangement (Laue case) of the specimens of quartz, KCl and NaClO₃ and to the reflection arrangement (Bragg case) of the specimens of Ge. In the transmission case, only thin specimens (about 0.3 mm thick) were used.

In the present work, crystal texture of LiF single crystals in as-grown state was investigated with this method, where this method was found to be applicable to thick specimens as well as thin specimens by the reason explained later.

The results are conveniently classified into two parts: the one on thin specimens (§ 3), and the other on thick specimens (§ 4). In § 3, special attention was paid to goniometric measurement on diffraction pattern concerning the resolution and the measurement of misorientation angle. In § 4, the inner structure is studied by X-ray topographic observation. Topographic as well as goniometric information was obtainable on photographs because of the profitable use of monochromatic convergent beam.

In both § 3 and § 4, observations by surface

etching were made before or after the X-ray photographic recording for better understanding of the diffraction pattern. LiF crystals were purchased from the Harshaw Chemical Company, Cleveland, Ohio.

§ 2. Experimental Method

The diffraction method is shown in Fig. 1. The crystal plate *M* used for the monochromator of transmission type is of quartz, 0.15 mm in thickness *t*, cut normal to the lattice plane (10 $\bar{1}0$) and bent elastically about the axis [0001] to a curvature of approximately $R=35$ cm in radius. Convergent beam of (20 $\bar{2}0$) diffracted MoK α_1 rays was used in the present work; a line focus of the width of

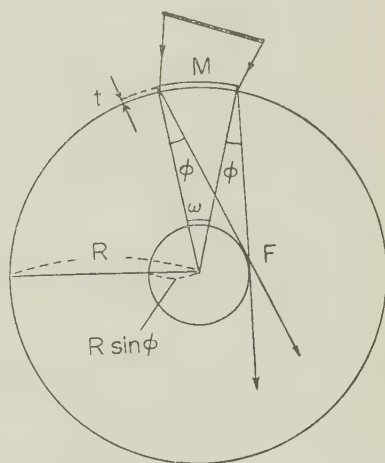


Fig. 1. Schematic illustration of the geometry of the diffraction method. ϕ , the angle between diffracting direction and the plane normal of the monochromator, is $9^{\circ}37' \equiv \theta_{(20\bar{2}0)}$. ω , the aperture of the monochromator, was taken as about 1° .

about 40μ was obtained at the focus F . The specimen was set at F and $K\alpha_2$ was cut off by a lead knife edge which was placed just in front of the specimen.

The vertical height a of the X-ray source was about 70μ in the take-off direction.

§ 3. Results on Thin Quartz and LiF Crystals

3.1. Diffraction patterns

As a preliminary work, a $(10\bar{1}0)$ transmission diffraction pattern was obtained by using a Brazilian quartz plate of thickness 0.39 mm , cut normal to $(10\bar{1}0)$, polished optically flat and etched in hydrofluoric acid. Along the pattern, a fairly good linearity and homogeneous intensity distribution were noticeable: the crystal irregularities were scarcely detected for the specimen which agreed with the result by Kato¹⁾

Fig. 2(a) is a (200) transmission diffraction pattern of a LiF crystal of thickness 0.51 mm . Surface (010) of the specimen remained cleaved. This is one of the typical patterns which were frequently observed in specimens cleaved off to a thickness of about 0.5 mm from a large single crystal of fairly high quality. Characteristics of the pattern are as follows.

(i) Linear regions extending over the length of the order of millimetre (a - b , b - c , ..., k - l , l - m).

(ii) Discontinuous steps (b , c , ..., k , l).

(iii) The border of the pattern is intense in parts: for instance, on one side from c to d and on both sides from a to b .

By means of etching observation, it was confirmed that each discontinuous step (ii) corresponds to a subgrain boundary. The shifting at a step depends on the type of the subgrain boundary and the degree of angular misorientation between neighbouring crystal-lites separated by it.

In Fig. 2(b), the specimen was annealed at 800°C for approximately 3 hours and etched in Gilman's Etch "A"²⁾. The thickness of the specimen was reduced to 0.45 mm by these treatments. The missing region indicated by A in the diffraction photograph is the shadow of a needle of 0.5 mm in diameter placed just at the back of the specimen to check the reflecting position. In comparison with Fig. 2(a), Fig. 2(b) shows:

(i') Increase of the linearity in the regions indicated in (i).

(ii') Increase of the sharpness of discontinuity at some steps.

(iii') Disappearance of the intense borders mentioned in (iii).

For the study of misorientation in crystal, parameters representing the misorientation are defined as follows.

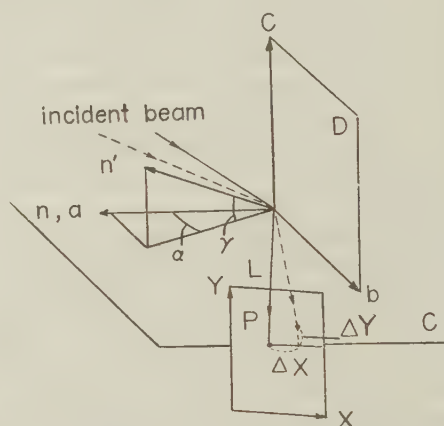


Fig. 3. Schematic illustration of misorientations. Relative misorientation angles are represented by parameters α and γ .

3.2. Relation between the misorientation and the step shift

The relation is illustrated in Fig. 3. The standard diffraction plane D is regarded as represented by vectors b and c , where a , b and c are orthogonal unit vectors. The plane normal vector n is parallel to a in this case. A slightly misoriented plane, if present, is characterized by a plane normal $n'(\alpha, \gamma)$, where α is the angle between a and the projection of n' on the plane C represented by a and b , and γ is the angle between n' and the plane C . A photographic film P is placed at a distance L from the specimen and perpendicular to the mean diffracting direction. The shift of the pattern reflected by the plane characterized by n' from that by n is expressed as

$$\Delta X = L\alpha \quad (1)$$

$$\Delta Y = 2\gamma L \sin \theta, \quad (2)$$

where the axis- Y is taken parallel to c , the axis- X is taken perpendicular to Y on the photographic film P , and θ is the Bragg angle.

The angular resolutions of the incident beam at the position of the specimen are

determined by the width b of the focus for the horizontal convergence and by the height a of the X-ray source for the vertical divergence. The resolution $\Delta\theta_{HC}$ for horizontal convergence is then expressed as $\Delta\theta_{HC}=b/R'$ and $\Delta\theta_{VD}$ for vertical divergence as $\Delta\theta_{VD}=a/(R'+Z)$, where R' is the specimen (focus)-to-monochromator distance and Z is the monochromator-to-X-ray source distance. The horizontal and vertical angular resolutions of the beam diffracted from the specimen are equal to $\Delta\theta_{HC}$ and $\Delta\theta_{VD}$ respectively if the broadening due to the specimen is not considered. Then the resolutions concerning α and γ are, by eqs. (1) and (2), $\Delta\alpha=\Delta\theta_{HC}$ and $\Delta\gamma=\Delta\theta_{VD}$ /

$2 \sin \theta$. In the present case, $b=40 \mu$, $a=70 \mu$, $R'=35 \text{ cm}$, $Z=8 \text{ cm}$ and $\theta=10^\circ 9'$ are used and we get $\Delta\alpha=24''$ add $\Delta\gamma=1'36''$. In order to improve the angular resolution on γ , a longer wavelength or a higher order reflection is desired. As a longer wavelength, however, results in a larger amount of absorption, a higher order reflection will be useful in this method.

3.3. Calculation of misorientation and interpretation of pattern characteristics

Measurements of misorientation were made on the photograph of Fig. 2(b). In Fig. 4(a), the part under consideration is shown magnified. The step shift at h suggests a twist-like misorientation of the part H_1 against the part H_2 . They are schematically drawn in Fig. 4(b). Misorientation measured from the right side of the border is $\alpha_1=42''$, that from the left side is $\alpha_2=46''$ and that from center-to-center is $\alpha_3=46''$. The part of diffraction pattern indicated by q was left out of consideration in measuring the twist angle at h for the reason explained later.

In Fig. 4(c), the subgrain boundary which played a role in producing a step shift at h in the diffraction photograph is shown. As schematically illustrated in Fig. 4(d), it is observed that the grain boundary plane is oblique to the plane (001) downward from the diffraction side (front in the figure) to the incident side (back in the figure) of the specimen, intersecting the crystal surface (010) by a line making an angle of 15° with the direction [100] and the crystal surface (100) by a line making an angle of $12^\circ 10'$ with the direction [010]. The angle between the normal N of the boundary plane and the direction [001] is then $17^\circ 50'$.

In order to see the correspondence between the misorientation angle derived from the structure of grain boundary dealt with in the dislocation theory and the misorientation measured from the diffraction photograph, we assume a twist-like model with square network of screw dislocations for this grain boundary and further assume that the real distribution of screw-like dislocations on this oblique grain boundary is the projection of ideal square network on the plane (001) in the directions [001]. In the ideal square network, two kinds of pure screw dislocations

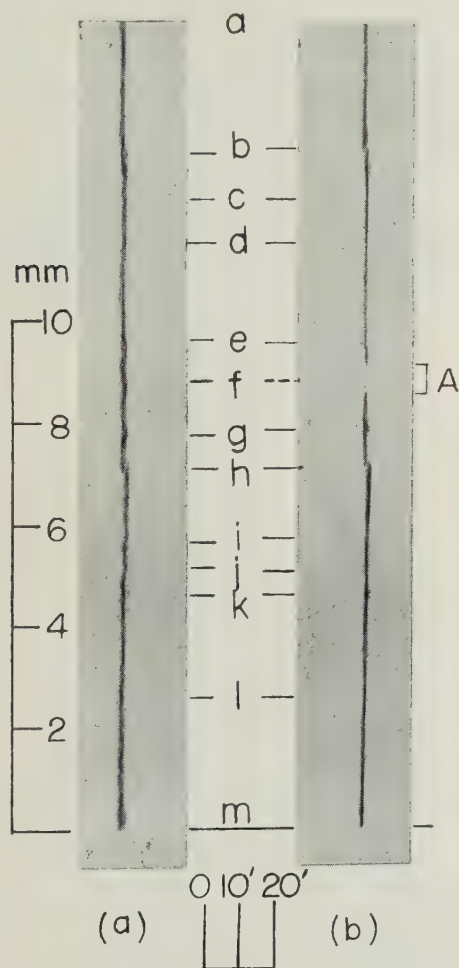


Fig. 2. (a): The diffraction pattern from the LiF single crystal of thickness 0.51 mm. Surface remains cleaved. ($L=50 \text{ cm}$). (b): The diffraction pattern from the same specimen annealed at 800°C for about 3 hrs. and etched. The thickness is 0.45 mm.

running in the directions $[\bar{1}\bar{1}0]$ and $[\bar{1}10]$ should have the same spacing h . In the real network, however, dislocations will not be of pure screw type and the spacings are not the same. The screw components of Burgers vectors then become $|b_{s1}|=0.95|b_s|$ for $[\bar{1}\bar{1}0]$ group and $|b_{s2}|=1.0|b_s|$ for $[\bar{1}10]$ group and the ratio of spacings become $h_1:h_2=1:1.06$, where $|b_s|$ is the magnitude of Burgers vector, $|a|[\bar{1}10]/2=2.84 \text{ \AA}$. These are conveniently averaged for the calculation of misorientation. After the correction for the tilt of the plane normal N in the direction $[001]$, we get the

relations between the mean distance d of etch pits and the angle α_B of twist about the axis $[001]$, which are listed in Table I. On Fig. 4(c) we get $d=0.83 \mu$ and $\alpha_B=47''$. The angle of misorientation measured on the diffraction photograph Fig. 4(a) is $\alpha_x=42''\sim 46''$. In this measurement a slightly tilted part of the pattern indicated by q was left out of consideration, for this was thought, by microscopic observation, to be due to another subgrain boundary plane in the crystal, branching off from the subgrain boundary under consideration and extending nearly parallel to

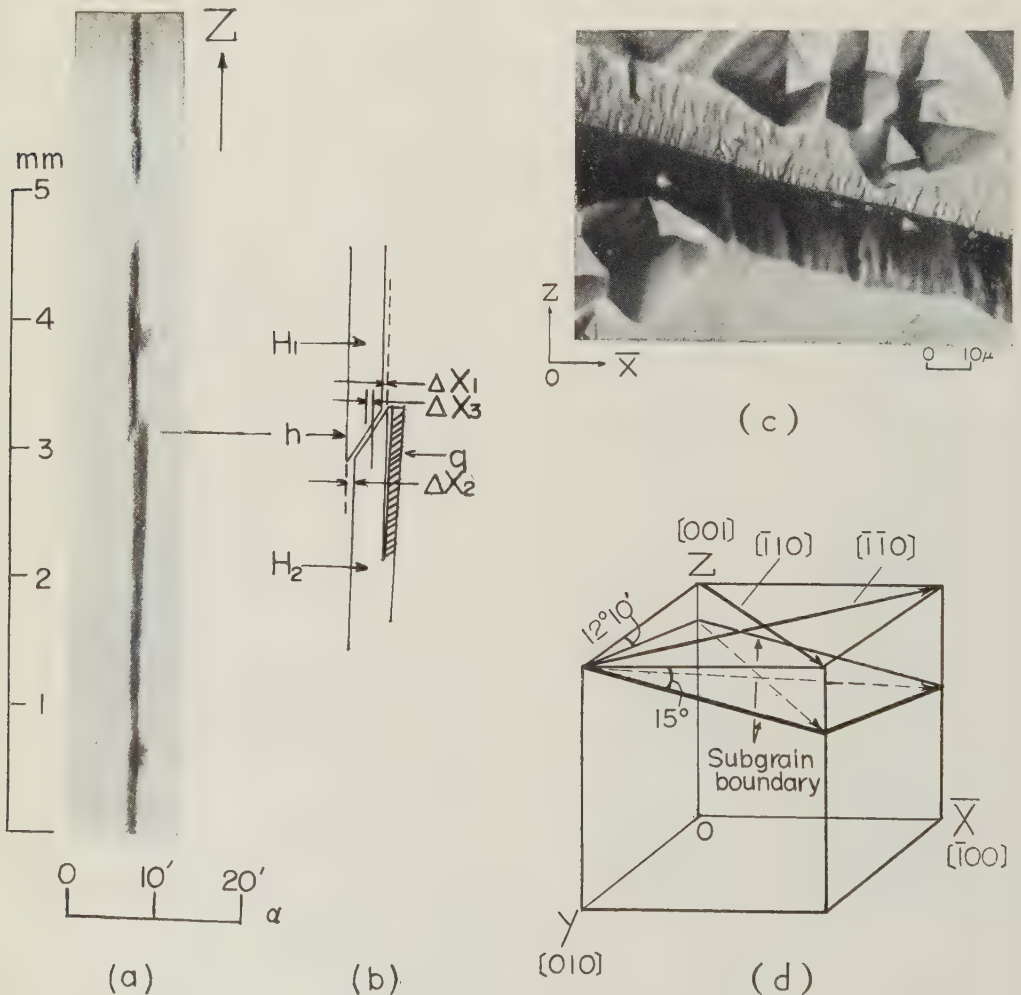


Fig. 4. (a): The enlarged photograph of the part h of Fig. 2(b). (b): Schematic illustration of the part h . (c): Part of the subgrain boundary which produced a step shift at h . (d): Direction of the subgrain boundary. Dotted arrow lines on the oblique subgrain boundary plane show the directions of two kinds of screw-rich dislocations. Full arrow lines on the plane (001) show the directions of pure screw dislocations making ideal square network.

the surface of the specimen.

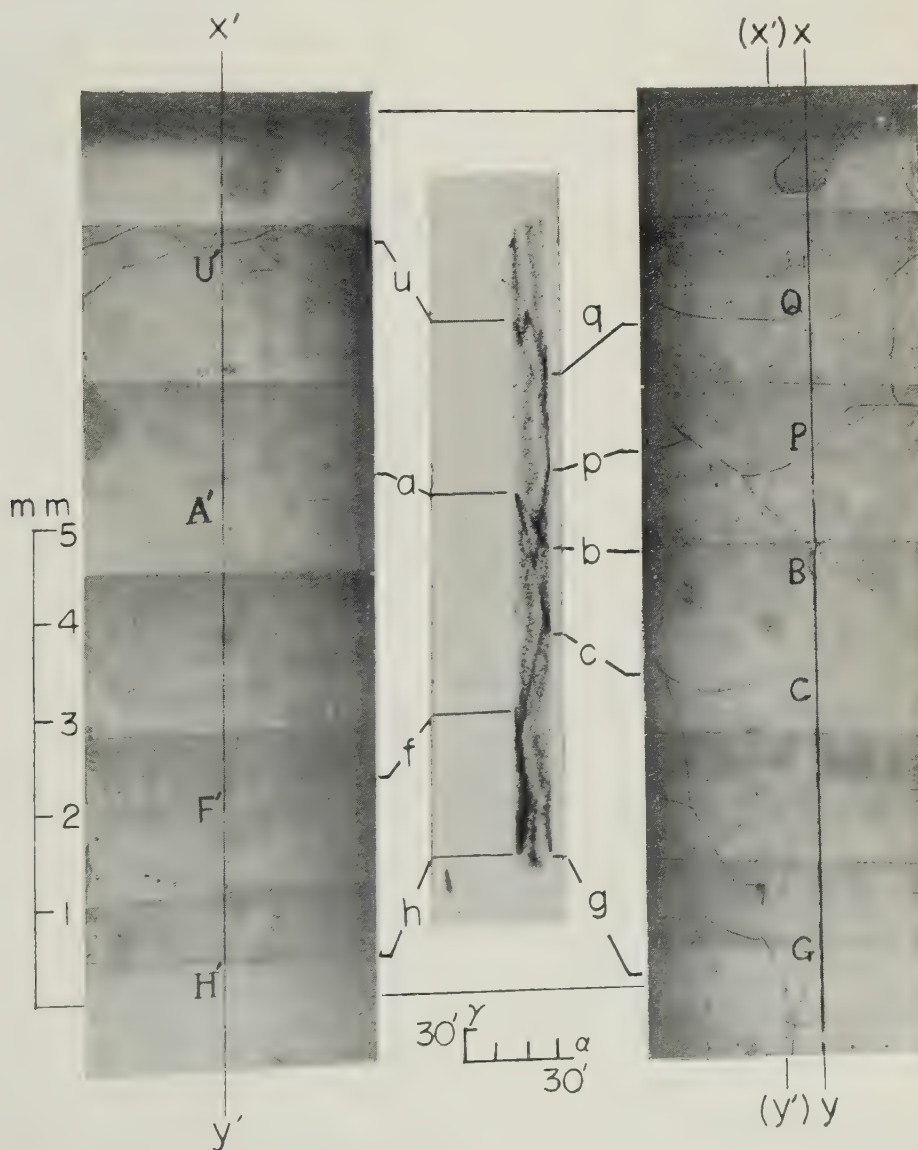
A fairly good agreement of α_F and α_X suggests the possibility to determine the type of the grain boundary by this X-ray method.

The intense appearance of the border of pattern (3.1, iii) is interpreted by the concept similar to that of the surface double spots⁴⁾ which were, in the present case, caused by partial cold work originating in cleaving but not by $K\alpha_2$ contamination, for $K\alpha_2$ was cut off completely.

It will be worth noting that the thickness of the specimen calculated by the simple rela-

Table I. The relations between the observed distance of etch pits on (010) surface and the calculated twist angle about the axis [001] for the subgrain boundary in Fig. 4 (d).

Mean distance of etch pits on (010) d (μ)	Twist angle about the axis [001] α_B (sec)
1	38.9
0.9	43.2
0.8	48.6
0.7	55.6
0.6	64.8



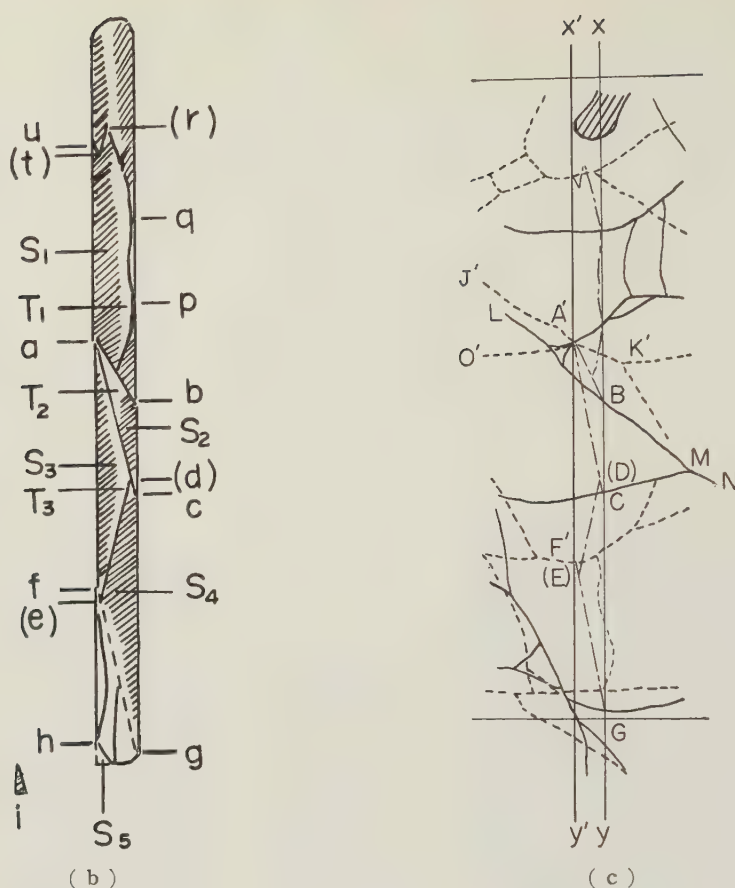


Fig. 5. (a): (200) diffraction pattern (at the middle) and the microscopic surface photograph of the specimen of thickness 2.2 mm. Irradiated linear parts are indicated by x - y on the diffraction side of the surface and by x' - y' on the incident side. Small letters refer to the positions on the diffraction pattern and the corresponding capital letters to the positions on the surface. They are connected by arrow lines. ($L=23$ cm). (b): Schematic illustration of the diffraction pattern. (c): Superposition of the subgrain boundaries and the inner strips shown on the diffraction pattern.

tion $t_{\text{calc}} = \delta/2 \sin \theta$, where δ is a mean distance of double lines (iii), is less by 0.14 mm than the actual thickness of the specimen. We consider then that the effective depth of the layer to produce intense reflection in the case of the surface being cold-worked is approximately 0.07 mm from the surface.

§ 4. Diffraction Patterns of Relatively Thick Crystals

4.1. Topographic information on the photograph

Fig. 5(a) shows a (200) diffraction pattern of a LiF single crystal of thickness 2.2 mm. The surfaces of the specimen were polished and etched with Gilman's Etch "A" prior to the recording of the diffraction pattern. The

crystal surface of diffraction side is placed on the right and that of incident side on the left printed reversed for convenience of comparison with the former. Arrow lines indicate their vertical positions. Irradiated narrow lines are indicated by the line connecting x and y on the diffraction side and by the line x' and y' on the incident side.

The inner fine structure of the diffraction pattern is illustrated schematically in Fig. 5(b). Some features are as follows:

(i) Narrow strips of anomalous intensity: dark (or positive) along the lines a - b , a - c and (d) - (e) and light (or negative) nearly along the line f - g .

(ii) Regions of uniform intensity (S_1 , S_2 , S_3 and S_4).

(iii) Narrow and blurred regions running along the side of the strips mentioned in (i) (T_1 , T_2 and T_3).

(iv) Small pattern i splitted from the part S_5 .

(v) Shift of the border of the pattern at a . (This will be shown in Fig. 8, for this is not clear in Fig. 5(a)).

Before interpreting these features, the topographic matching of diffraction pattern (denoted hereafter by DP) with the surface photograph (denoted by SP) was carried out. It was found by the vertical correspondence in Fig. 5(a) that points a , b , c and f on the border of the DP correspond to the points where the incident X-ray sheet cuts subgrain boundaries on each surface. These points are marked by capital letters on SP s, (with primes on the incident side), corresponding to small letters on the DP .

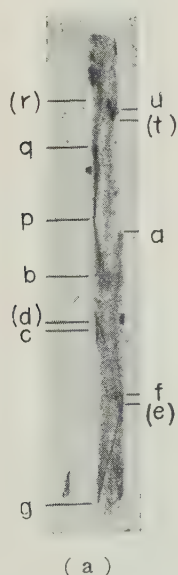
In Fig. 5(c), two SP s are superposed and subgrain boundaries on the diffraction side are traced by full lines, while on the incident side by dotted lines. In this figure, the narrow strips of anomalous intensity $a-b$ etc. (i) are shown by chain lines, matching a , b , c , f and g with A' , B , C , F' and G respectively, and (d) and (e) with (D) and (E) by proportional calculation respectively where bracket

refers to the inner point of the specimen.

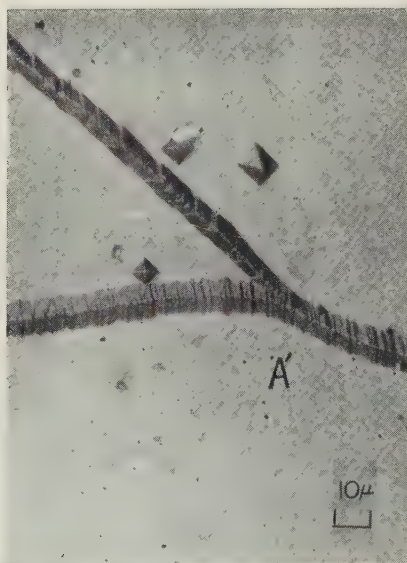
Thus, it is suggested that the lines $a-b$ etc. in the DP are the projections of the intersection lines of subgrain boundaries with the incident X-ray sheet in the specimen. They are, then, understood to be the topographic images in the sense of Lang's work⁵⁾ and we can now determine the boundary configurations in the specimen with the help of observation on SP . For instance, lines $a-b$ and $a-c$ start from the point a on the border of DP and the X-ray sheet cuts a branch node A' of the subgrain boundaries on the incident side of SP . This means that subgrain boundaries $J'A'$ and BM make a boundary plane in the specimen, and $O'A'$ and CM make a boundary plane. Branch node A' runs to M through the specimen. (D) and (E) mean the branching of boundaries in the specimen.

4.2. Origin of the intensity distribution of topographic image

In Fig. 6(a), the diffraction pattern ($\bar{2}00$) was taken by reversing the specimen of Fig. 5(a) by 180° . It will easily be understood in this case that the topographic configurations in DP change almost mirror-symmetrically against the initial (Fig. 5(a)). It is noticeable that dark lines $a-b$, $a-c$ and $(d)-(e)$ have changed into light and, on the other hand,



(a)



(b)

Fig. 6. (a): ($\bar{2}00$) diffraction pattern from the same regions of the specimen of Fig. 5 (a). Specimen is arranged reversed against Fig. 5 (a). (b): Subgrain boundary in the vicinity of A' of Fig. 5 (a).

line $f-g$ has become dark which was initially light while the contrasts of parts of $p-q-(r)-(t)-u$ are unchanged.

In order to make clear the character of the boundaries which produced the lines $a-b$ and $a-c$, the SP in the vicinity of A' in Fig. 5(a) is shown in Fig. 6(b) in larger magnification.

Figs. 7(a) and 7(b) show DP's of another specimen with cleaved surfaces of thickness 0.7 mm. They are recorded reversed to each other. In this case, however, the changes in contrast are scarcely observable: w , x and z did not change while v changed. The grain boundary corresponding to the unchanged intensive region w is shown in Fig. 7(c).

The effects of a grain boundary on the dif-

fraction pattern are classified into two: the first, the misorientation of a grain to the adjoining grain separated by the grain boundary; the second, the lattice defects on the boundary itself. On reversing the setting of the specimen for recording, the first effect will result always in reversing of the contrast: ΔX does not change in sign but topographic configuration changes mirror-symmetrically and ΔY changes in sign. The second effect results in a reduction of the primary extinction and therefore dark (positive) contrast may be always expected.

Thus, for explaining the results obtained above, two effects are considered possible in LiF crystals: in the case of Figs. 5(a) and 6(a) the misorientation effects are dominant and in the case of Figs. 7(a) and 7(b) the effect of reduction of extinction is explicitly observed. Two instances mentioned above are, however, rather extreme cases and we consider that some reduction of extinction must always occur where the lattice defects such as grain boundary are present. Difference between the grain boundary effects in two

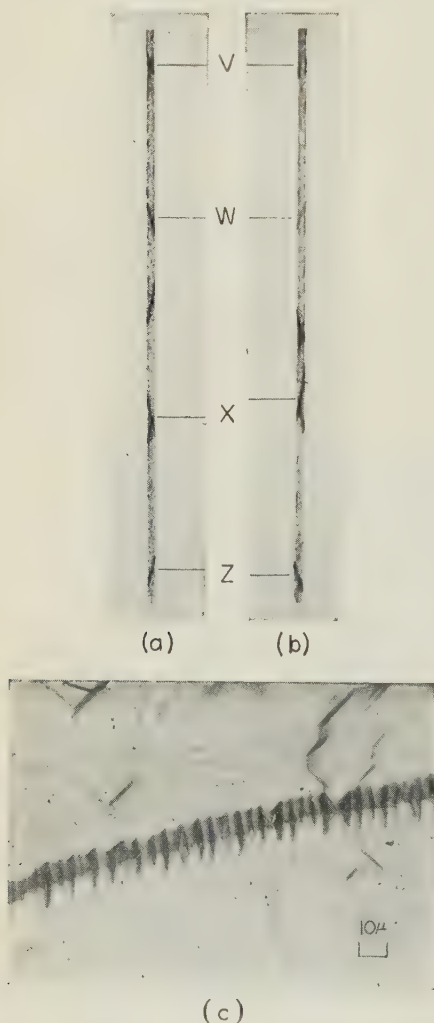


Fig. 7. (a) and (b): (200) and $(\bar{2}00)$ diffraction pattern from the LiF plate of thickness 0.7 mm. (c): Subgrain boundary corresponding to the part w in Figs. 7(a) and (b).

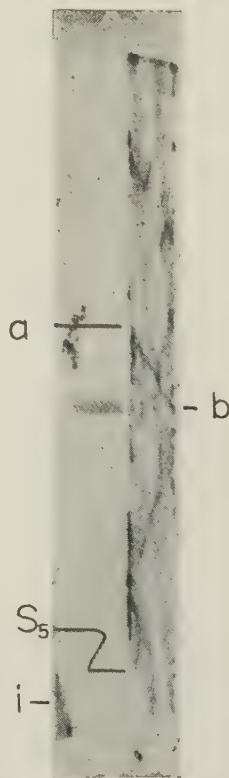


Fig. 8. (200) diffraction pattern from the same regions as in Fig. 5(a), but the surface of the specimen remains cleaved. Thickness is 2.8 mm.

instances is considered due mainly to the magnitude of misorientation.

In comparison between subgrain boundaries of Fig. 6(b) and 7(c), the average distance of etch pits is less than 1μ in the former and is 3μ in the latter. The misorientation was calculated for the subgrain boundary in the latter as $\alpha=15''$ at the most by assuming the ideal twist grain boundary. For such a small angle boundary, where the misorientation angle of diffracted rays from two subgrains separated by this boundary is less than the resolution, the effect of reduction of extinction is considered more likely to produce the dark (positive) contrast along the narrow strips, say w , in Fig. 7(a) and 7(b) than the effect of misorientation.

Corresponding to the regions of uniform intensity (4.1 ii), random etch pits of about 10^4 cm^{-2} are counted on the *SP*. Images of single dislocation lines such as pointed out by Lang⁶⁾ are not observed probably because of low resolution.

In the vicinity of subgrain boundaries on the *SP*, random etch pits density is lower in general than that in the interior of grains. Blurred regions running along the side of strips (4.1 iii) are, therefore, considered to correspond to the better regions near the boundaries.

4.3. Goniometric information on the photograph

Returning to Fig. 5(a), the small pattern i (4.1 iv) and the shift of the border at a (4.1 v) are the direct goniometric information as obtained in § 3. For the calculation of misorientation Eqs. (1) and (2) are applied. The resolving power of misorientation angle is, however, reduced owing to the blurred border: etching treatment dulled the sharpness of the border. For the observation of the border of *DP*, specimens with cleaved surface are rather useful.

In Fig. 8, the same *DP* as Fig. 5(a) is shown with the surface of the specimen in freshly cleaved state*. The thickness of the specimen was 2.8 mm. The border of *DP* is sharp and intense in parts. From the measurable shift at a and b , the misorientation at the boundary $a-b$ was calculated as $\alpha=48''$ and γ is order of $1'$. At the highly misoriented pattern i which was splitted from the part

S_0 , $\alpha=23'$ and $\gamma=12'$ were obtained.

§ 5. Conclusion

The convergent beam method is sensitive both to the misorientation angle and to the position of reflecting crystal element within a narrow linear region; we can designate the part of a specimen for observation and determine the magnitude of the misorientation angle between adjacent subgrains and the dimension of them with high accuracy, holding the point-to-point correspondence between the specimen and diffraction pattern, as shown in Figs. 2 and 4 for the thin specimen and in Fig. 5(a) for the thick specimen. The magnitude of the misorientation between adjacent subgrains determined by the present method of X-ray shows the good agreement with the one determined from the etch pits pattern by referring to the dislocation theory.

Specimens used here contained subgrains 1 mm average dimension with misorientation of about 1 minute. Dislocation density in subgrains was approximately $5 \times 10^4\text{ cm}^{-2}$.

As the new possibility of this method it is shown that the topographic as well as goniometric information is obtainable in a diffraction photograph as seen in Fig. 5(a).

In this work, however, the direct observation of random dislocations was not possible probably because of their dense distribution in crystals and the coarse grain of photographic emulsion. If adequate crystals were provided, the present method would enable the direct observation.

In conclusion, the author expresses his sincere thanks to Prof. Einosuke Fukushima for his guidance throughout this work and to Prof. Akiya Ookawa for his helpful discussions.

This work was supported by the Scientific Research Fund granted by the Ministry of Education.

References

- 1) N. Kato: *Acta Met.* **5** (1957) 237; **6** (1958) 647.
- 2) H. Lambot, L. Vassamillet and J. Dejae: *Acta Met.* **1** (1953) 711; **3** (1955) 150.
- 3) J. J. Gilman and W. G. Johnston: *Dislocations and Mechanical Properties of Crystals* (John Wiley, 1957) 116.
- 4) Y. Sakisaka and I. Sumoto: *Proc. Physico-Mathematical Soc. of Japan* **13** (1931) 211.
- 5) A. R. Lang: *Acta Met.* **5** (1957) 358.
- 6) A. R. Lang: *J. Appl. Phys.* **29** (1958) 995.

* Fig. 8 was recorded before Fig. 5(a).

The Theory of the Fine Structure of the X-ray Absorption Spectrum, II.

By Toshio SHIRAIWA

Faculty of Science, Osaka University

(Received August 24, 1959)

In the interpretation of the fine structure of the x-ray absorption spectrum in solids, the life time of the state of the electron ejected by a photon is considered. With the assumption that the inelastic cross section of collision between the electron and an atom has a magnitude of the order of one square Angstrom, Kronig's method for molecules is applied to solids in order to obtain the variation of the transition probability. The wave function of the final state of the transition is obtained as the sum of the plane wave, whose amplitude decreases with increasing distance from the atom which ejected the electron, and the waves scattered by the neighboring atoms. The scattering amplitude is calculated numerically for the Hartree field of the atom. Calculations are applied to the *K*-absorption spectra of copper and titanium and to *K*-absorption spectra of titanium in the two modifications of titanium dioxides, rutile and anatase. The calculated results agree well with experiments in copper and titanium, and the agreements become worse in titanium dioxides.

§ 1. Introduction

When x-rays transmit materials, the inner electrons in the atoms are excited and the absorption of the x-rays occur. The electrons are excited to empty levels lying above the Fermi distribution, and so the absorption coefficient increases abruptly at the corresponding wave-length, which is called an absorption edge. The absorption spectrum is called *K* or *L* absorption spectrum according to the level of the electron which causes absorption. At the shorter wave-length side of the edge, the absorption coefficient does not change monotonically but shows a fine structure. A fine structure is observed in molecules and solids. Especially, it extends several hundreds of electron volts in metals.

The fine structure of solid has been explained by Kronig¹⁾ as follows. The empty levels lying above the Fermi surface are grouped into allowed and forbidden bands, and the density of states and the transition probability to them are not monotonic functions of the energy. The absorption coefficient is proportional to the product of these two quantities, and will therefore show a fine structure. In Kronig's calculation the electron is treated as an nearly free and the potential of ions in the crystal is treated as an perturbing potential. The energy gap of states

occurs at the boundary of the Brillouin zones. Kronig calculated the variation of the density of states and neglected the variation of the transition probability. The result of the calculation predicts much more fine structure than experiment reveals. For the comparison with the experimental result, he proposed a graphical representation. The anomalies of the density of states were suitably grouped in the density curve and, by such grouping, he explained the positions of absorption maxima and minima of the fine structure.

The result according to the method proposed by Kronig did not coincide with experiment, and after him several theories based on the different standpoints have been published²⁾. The abstracts of these theories were referred in the present author's previous³⁾ report (Report I).

In these theories, the most acceptable one is Kronig's theory and discrepancy between results of theory and experiment will be due to the simplification of the calculation and to the factors neglected in his calculation. In order to develop the calculation according to Kronig and to interpret the experimental results quantitatively, one must consider following points. In Kronig's computation of the eigenfunction of an electron, only the degeneracy of two states is considered near

the discontinuous plane of the energy in the wave number space, but it is necessary to consider the more degeneracy near the cross lines and points of these discontinuous planes. These cross lines or points increase rapidly in number in the high energy region, so that the form of the zone must be changed considerably. Secondly the calculation of the transition probability must be included. In insulators it will be necessary to consider the effect of the potential due to the inner electron missing. Also the spreading of the absorption band which is corresponding to the life time of the excited state, must be considered. These calculations, especially, to obtain the precise density of states and the transition probability to them, are very tedious.

However, it is possible to interpret the fine structure quantitatively by the more easy method which can be done through a simplified calculation, having been shown in the first report³⁾. This method is based on the following theoretical standpoint. In the process of the transition of an electron which absorbs a photon energy and jumps to the nearly free space, the wave packet is formed corresponding to uncertainty of the energy and the wave packet spreads with time. At the same time the amplitude decreases with its life time, and if the life time is sufficiently small the wave packet does not extend so far from the excited atom. The wave function is a solution of the time dependent Schrödinger equation for the initial condition that the function is that of the inner level, and the potential field which determines the wave function is the potential in the wave packet. Thus, if the life time is small, the transition problem in a crystal can be replaced by a problem in a small space around the atom which absorbs a photon.

The amplitude of the ejected electron decreases due to the inelastic collisions with atoms in the crystal. A slow electron can penetrate only a few atomic layers and also it is perhaps not so wrong to assume that the inelastic cross section is larger than one square Angstrom. Then, it becomes possible to adopt a method which has been used by Kronig and others⁴⁾ to interpret the fine structure of gas molecule. In this method the ejected electron was approximated as a sum of a plane wave and the waves scattered

by the partner atoms and the variation of the transition probability from the K state was obtained. In the solid the ejected electron decreases by inelastic collisions with neighboring atoms and this method can be applied to solids.

In the first report, calculations according to this principle were applied to K absorption spectra of iron, nickel and copper and good results were obtained. But in the calculation, simplifications were done. The potential of an atom was assumed as one of a well type and the Born scattering formula was used, and a radius of a potential hole was determined so as to give the best fit to the experimental result. These simplifications are rough approximations and in the present paper the scattering amplitude has been obtained numerically for Hartree's field. The effect of the missing K electron on the potential field was neglected. Calculations in the present paper have been done in order to interpret the fine structure in higher energy region than a few tens of electron volts from the edge. In the above region the free electron approach can be used and simplifications of the calculation were done. The calculations have been applied to the K absorption spectra of copper, titanium and titanium in the two modifications of titanium dioxides, rutile and anatase. The results were in good agreements with experiments in metals.

§ 2. Calculation

An electron in a free space can be expressed by a series of a plane waves,

$$\exp(ikr), \quad (1)$$

and in the present case, let us replace it by

$$\psi_i = \exp\left(-\frac{\mu}{2}r + ikr\right), \quad (2)$$

where $k/2\pi$ is the wave number vector. μ is the absorption coefficient of the electron and is related to the cross section between an electron and an atom by the equation

$$\mu = \rho\sigma_t = \rho(\sigma_{inel} + \sigma_{el}), \quad (3)$$

where σ_t is the total cross section, σ_{inel} and σ_{el} is the inelastic and elastic cross section and ρ is the number of atoms per unit volume.

The wave function of the ejected electron is represented by

$$\psi = \psi_i + \sum_s \psi_s, \quad (4)$$

where ψ_s is the wave scattered by the neighboring s -th atom. In Eq. (4) the multiple scattered waves are neglected but if σ_{inel} is small these terms must be considered and the result gives the eigenfunction in the whole crystal. In this case Kronig's method for solids will be more suitable.

The wave scattered by a potential hole $V(r)$ for an incident plane wave is represented asymptotically by the next formula⁵⁾

$$\frac{1}{r} \exp(ikr) \cdot f(\theta),$$

$$f(\theta) = \sum_{l=0}^{\infty} \frac{1}{2ik} (2l+1) \{ \exp(2i\eta_l) - 1 \} P_l(\cos \theta), \quad (5)$$

where η_l is the phase of the scattered spherical wave.

By the same procedure in Report I and using the formula (5) when incident x-rays are unpolarized and the absorber of the x-rays is an assembly of fine crystals, the fluctuating term of the transition probability from a 1s state to the state, whose wave function is represented by Eq. (4), is proportional to the following quantity, which represents the ratio of the fluctuating term of the transition probability to that of the isolated atom,

$$\sum_s N_s \frac{2\pi}{k^2 r_s^2} \exp(-\mu r_s) \times \{ -\sin 2kr_s \sum_l (-1)^l (2l+1) \sin 2\eta_l + \cos 2kr_s \sum_l (-1)^l (2l+1) (\cos 2\eta_l - 1) \}, \quad (6)$$

where the interference terms between scattered waves are neglected and N_s is the number of atoms which are at equal distance r_s from the centered atom, and summation extends all over the different r_s . In the present calculation the vicinity of the absorption edge is excluded and terms of higher order of $1/kr$ is neglected in the expression (6) as in Report I. The state density is assumed that it is proportional to k as in the case of an isolated atom. Then the fluctuation of the absorption coefficient is proportional to the quantity (6) multiplied by k ,

$$X = \sum_s N_s \frac{2\pi}{k r_s^2} \exp(-\mu r_s) \times \{ -\sin 2kr_s \sum_l (-1)^l (2l+1) \sin 2\eta_l + \cos 2kr_s \sum_l (-1)^l (2l+1) (\cos 2\eta_l - 1) \}. \quad (7)$$

The phases η_l which occur in expression

(5) are determined in the following ways⁵⁾. Let $G(r)$ be the bounded solution of

$$\frac{d^2 G}{dr^2} + \left[k^2 - \frac{2m}{\hbar^2} V(r) - \frac{l(l+1)}{r^2} \right] G = 0. \quad (8)$$

For larger r , G will have the asymptotic form

$$G \sim \sin \left(kr - \frac{1}{2} n\pi + \eta_l \right),$$

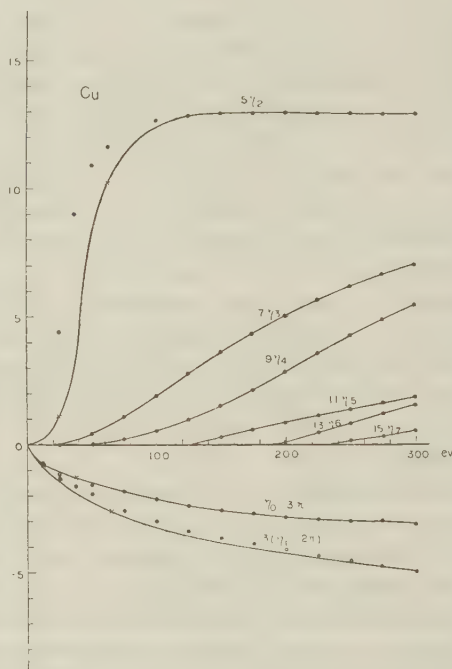


Fig. 1. Showing phases η_l of the electron wave scattered by a copper ion. The dotted points are the results according to Eq. (9) and cross points are the results obtained from the numerical solution of Eq. (8).

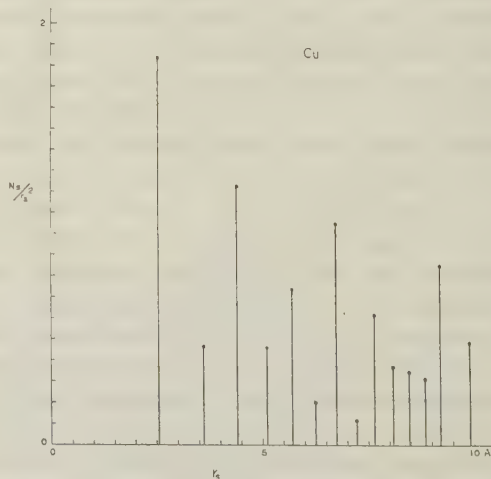


Fig. 2. Showing distribution of neighboring atoms in copper. N_s is number of atoms whose distances are r_s from the centered atom.

and then η_l is obtained. When the potential is large but does not vary much in a wavelength, the following expression can be used

$$\eta_l = \int_0^\infty \left\{ k^2 - \frac{2m}{\hbar^2} V - \frac{l(l+1)}{r^2} \right\}^{1/2} \times dr - \int_0^\infty \left\{ k^2 - \frac{l(l+1)}{r^2} \right\}^{1/2} dr, \quad (9)$$

where the lower limit of the integral in each case is the zero of the integrand. In obtaining η_0 , the term, $l(l+1)$, is substituted by $(l+\frac{1}{2})^2$, having been shown by Langer⁶⁾.

§ 3. Results of Computations

Copper

The numerical values of the potential field of a copper ion were referred to Hartree⁷⁾. The phase η_l was obtained by using Eq. (9) in the high energy region. In the lower energy region and for small value of l , it was obtained from the numerical solution of Eq. (8). The method of the numerical calculation was followed that of Shibagaki⁸⁾. The values of η_l are in Fig. 1. In the figure the dotted

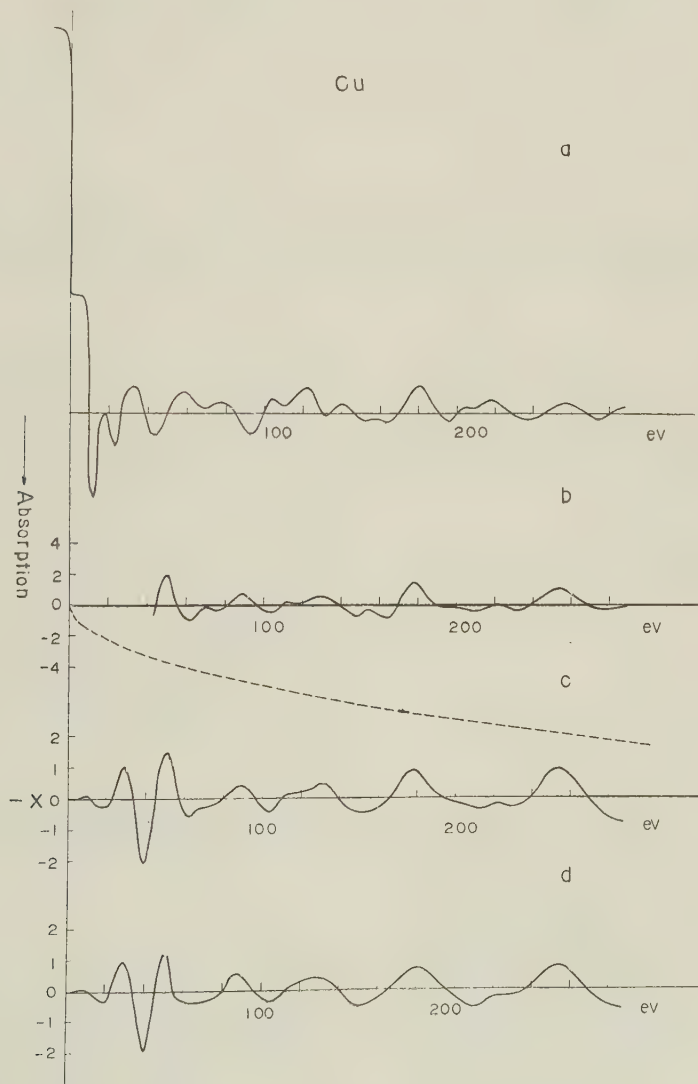


Fig. 3. The fine structure of the x-ray absorption spectrum of copper at the K absorption edge. a is the experimental curve and b , c and d is the calculated curve when μ is equal to 0.069, 0.138 and 0.277 $\text{\AA}^{-1}$ respectively. A dashed line represents $k=2\pi\sqrt{E/150}$. Summation in (7) extends over values of r_s to 10 $\text{\AA}$.

points are the results according to Eq. (9) and cross points are the results according to the latter method.

The values of N_s/r_s^2 , where N_s is the number of the neighboring atoms whose distances from the centered atom are r_s , are shown in Fig. 2.

Fig. 3 shows the calculated values of the quantities (7) for assumed three values of μ , 0.069, 0.138 and $0.277\text{\AA}^{-1}$ which are corresponding to that the ejected electron decreases to $1/e$ as it moves a distance $\frac{1}{2}$, 1 or 2 times of the lattice constant, respectively. For the comparison of the results calculated on the

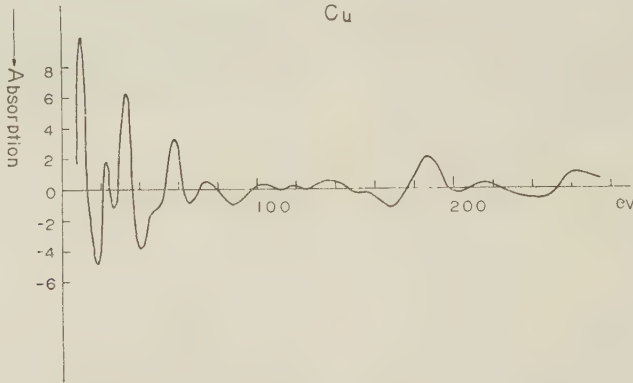


Fig. 4. The fine structure of the x-ray absorption spectrum of copper at the K absorption edge calculated according to the method in Report I. The value of μ is zero and summation extends to the 7-th neighbors. The radius of the potential hole is assumed to be 0.42 $\text{\AA}$.

assumptions of the potential hole of a well type and the Born scattering formula, the results of Report I are shown in Fig. 4, where μ is equal zero and a radius of a potential hole is 0.42 $\text{\AA}$.

Titanium

An analytical formula of the potential of a titanium atom has been obtained by Löwdin

and Appel⁹⁾, but in the present calculation it was obtained from distribution of electrons according to the Slater rule¹⁰⁾ in order to simplify the calculation. Values of η_l obtained by using the formula (9) are in Fig. 5. The crystal structure of titanium is close packed hexagonal and the values of N_s/r_s^2 are shown in Fig. 6. Fig. 7 shows the results of the present calculation. The values of μ are $1/12$, $1/6$ and $1/3 \text{\AA}^{-1}$ respectively. Fig. 8 shows the result of the simplified calculation according to Report I, where μ is equal to zero and the radius of a potential hole is 0.48 $\text{\AA}$.

Rutile and Anatase

The numerical values of the potential field

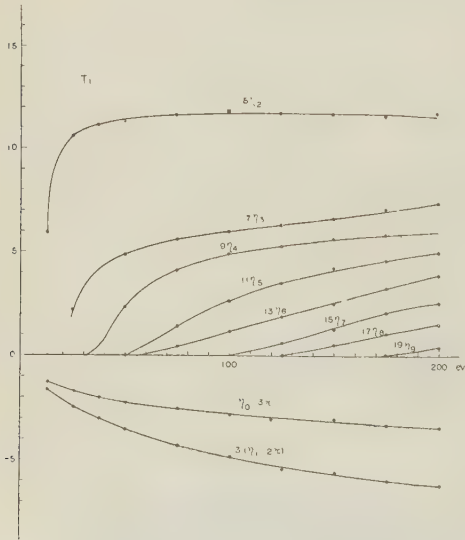


Fig. 5. Showing phases η_l of the electron wave scattered by a titanium atom.

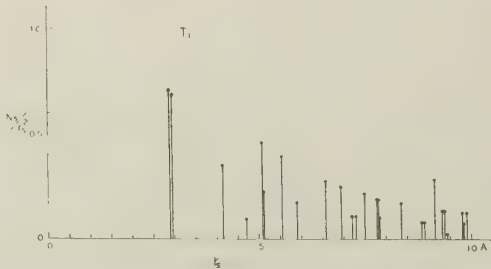


Fig. 6. Showing distribution of neighboring atoms in titanium. N_s is number of atoms whose distances are r_s from the centered atom.

of an oxygen atom were referred to Hartree¹¹⁾. The calculated values of phases are shown in Fig. 9. They were obtained by using Eq. (9). The calculation was applied to rutile and anatase. Their crystal structure were referred to Schossberger and others¹²⁾. The distribution of the neighboring atoms, N_s/r_s^2 , are shown in Fig. 10 and Fig. 11. In these figures vertical lines with dotted points represent oxygen atoms and those with cross points represent titanium atoms. Fig. 12 and Fig. 13 show the calculated results of the quantity

(7) in the cases of rutile and anatase respectively.

Agreements between calculations and experiments are worse than those in the case of metals. The reason is suggested to be due to the free electron approach used in the calculation and to the neglect of the potential change of the missing K electron.

Note on the applicability of the calculation.

In figures of the fine structure, the value of the ordinate is $-X$, which represents the ratio of the fluctuating term of the transition

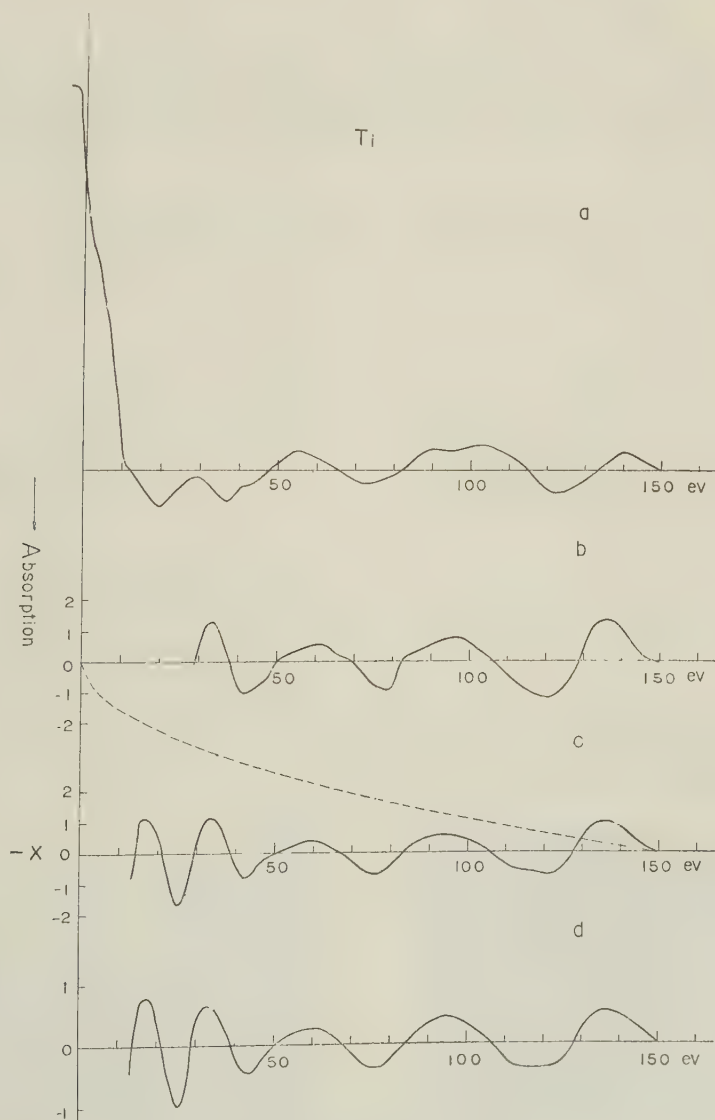


Fig. 7. The fine structure of the x-ray absorption spectrum of titanium at the K absorption edge. a is the experimental curve and b , c and d is the calculated curve when μ is equal to $1/12$, $1/6$ and $1/3$ $\text{\AA}^{-1}$ respectively. A dashed line represents $k=2\sqrt{E/150}$. Summation in the formula (7) extends over values of r_s to 10 $\text{\AA}$.

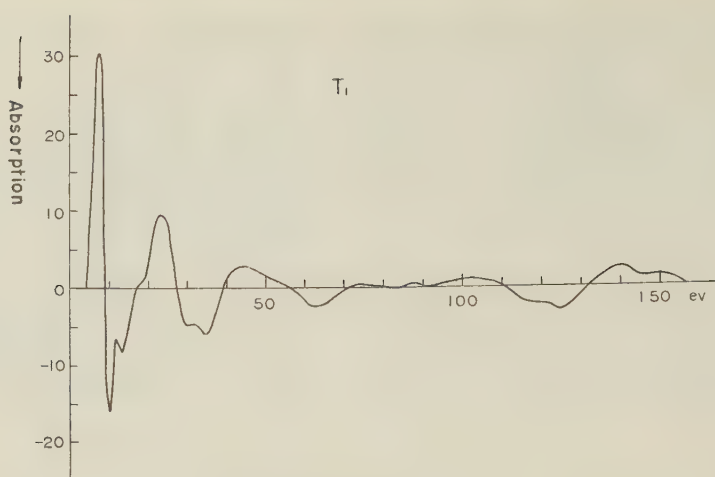


Fig. 8. The fine structure of the x-ray absorption spectrum of titanium at the *K* absorption edge calculated according to the method in Report I. The value of μ is zero and summation extends to the 7-th neighbors. The radius of the potential is assumed to be 0.48 Å.

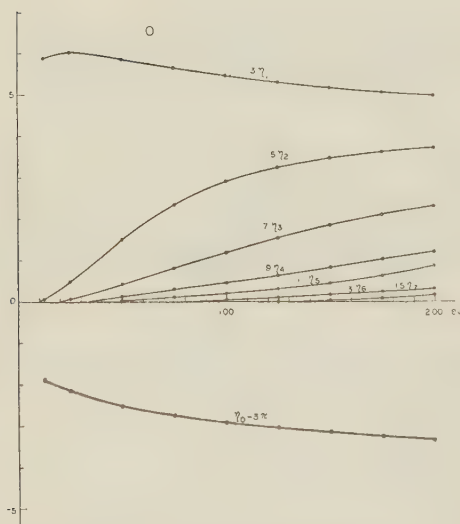


Fig. 9. Showing phases η_l of the electron wave scattered by an oxygen atom.

probability of solid to that of the isolated atom multiplied by k and the dimension is k . A dashed parabola inserted in the uppermost figure of the calculated curves represents

$$k = 2\pi \sqrt{\frac{E}{150}}$$

where E is expressed in ev and k is expressed in $1/\text{Å}$, and so it represents the absorption curve corresponding to the isolated atom. When the fluctuation of the calculated curve crosses over this line, the present calculation is meaningless and terms of interference

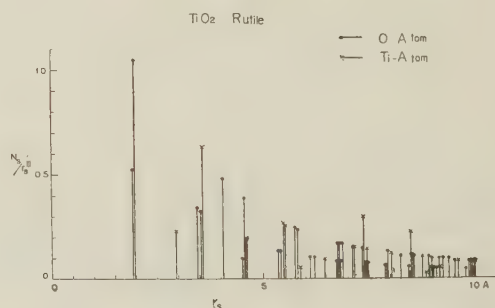


Fig. 10. Showing distribution of neighboring atoms around a titanium atom in rutile. Dotted points represent oxygen neighboring atoms and cross points represent titanium neighboring atoms. N_s is number of atoms whose distances are r_s from the centered atom.

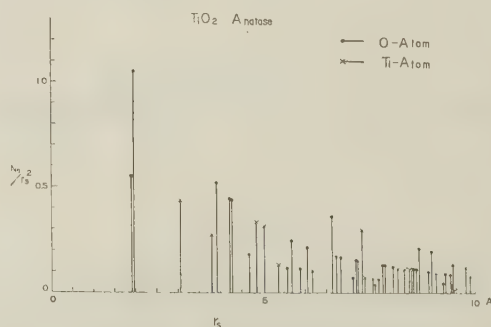


Fig. 11. Showing distribution of neighboring atoms around a titanium atom in anatase. Dotted points represent oxygen neighboring atoms and cross points represent titanium neighboring atoms. N_s is number of atoms whose distances are r_s from the centered atom.

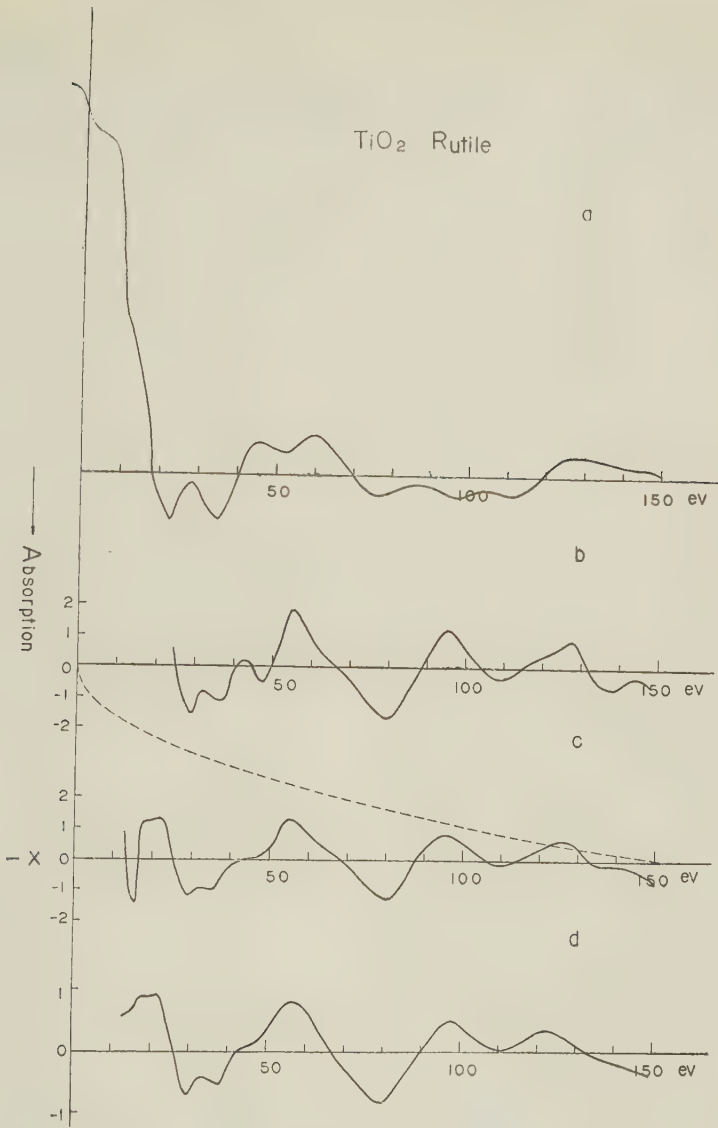


Fig. 12. The fine structure of the x-ray absorption spectrum of titanium in rutile at the *K* absorption edge. *a* is the experimental curve and *b*, *c* and *d* is the calculated curve when μ is equal to $1/12$, $1/6$ and $1/3 \text{ \AA}^{-1}$ respectively. A dashed line represents $k=2\pi\sqrt{E/150}$. Summation in the formula (7) extends over values of r_s to $10 \text{ \AA}$.



Photo. I. Photometer curve of *K* absorption spectrum of metallic titanium. About twenty curves are recorded to eliminate effect of grains.

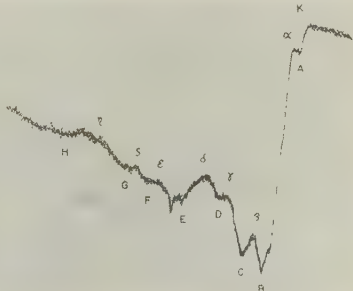


Photo. II. Photometer curve of titanium *K* absorption spectrum of rutile. About twenty curves are recorded to eliminate effect of grains.

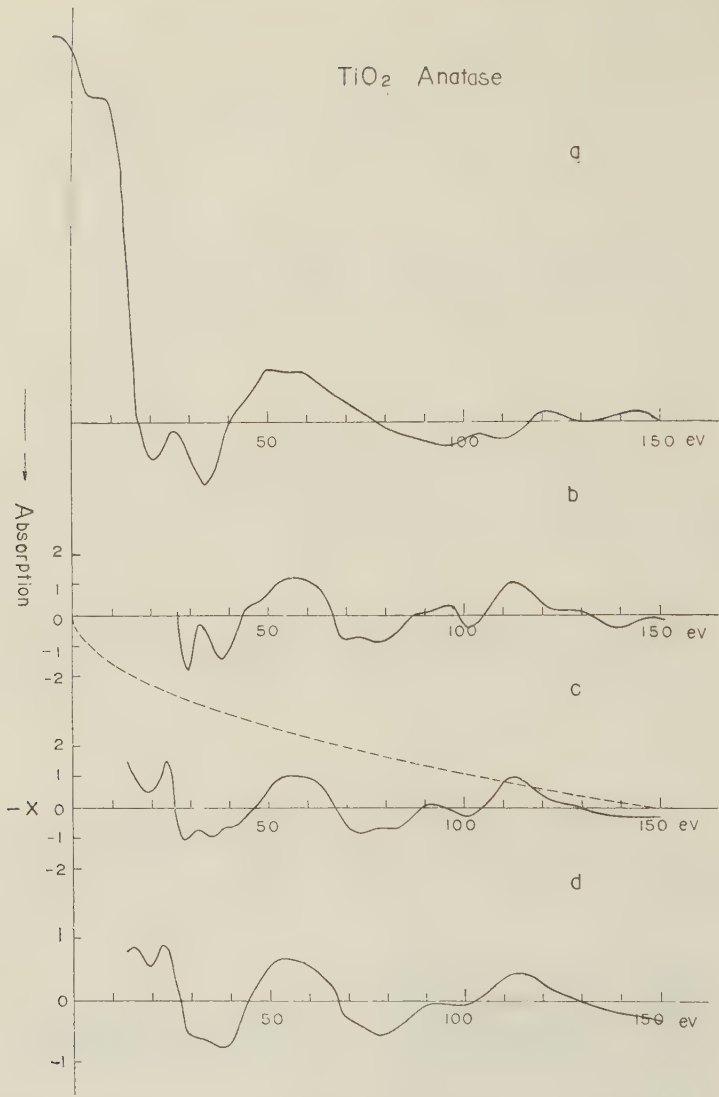


Fig. 13. The fine structure of the x-ray absorption spectrum of titanium in anatase at the *K* absorption edge. *a* is the experimental curve and *b*, *c* and *d* is the calculated curve when μ is equal to 1/12, 1/6 and 1/3A⁻¹ respectively. A dashed line represents $k=2\pi\sqrt{E}/150$. Summation in the formula (7) extends over values of r_s to 10 Å.

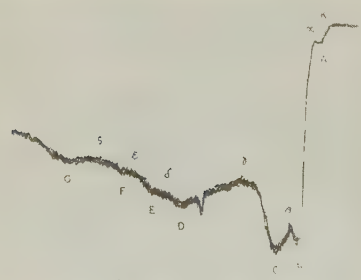


Photo. III. Photometer curve of titanium *K* absorption spectrum of anatase. About twenty curves are recorded to eliminate effect of grains.

between scattered waves and multiple scattered waves must be considered. Such region appears in the low energy region and in the case of small value of μ , and the calculated curve in the region is not described in the figure.

§ 4. Experimental Results of Absorption Spectra of Titanium and Titanium dioxides

Absorption spectra of titanium and titanium dioxides, which are compared with the calculated results in Figs. 7, 8, 12 and 13, have

Table I. Wave-lengths and energy separations of absorption maxima and minima in the fine structure of titanium *K* absorption spectrum of metal.

	Wave-length in x.u.	Energy separation in ev.
Edge	2492.3	
A	2483.3	18
α	2477.2	30
B	2474.0	36
β	2465	54
C	2457	71
γ	2442	103
D	2433	120
δ	2424	140

Table II. Wave-lengths and energy separations of absorption maxima and minima in the fine structure of titanium *K* absorption spectrum of rutile.

	Wave-length in x.u.	Energy separation in ev.
Edge	2490.9	
A	2490.0	1.9
α	2488.0	5.6
B	2480.1	22
β	2477.3	27
C	2473.9	34
γ	2469	45
D	2466	50
δ	2462	58
E	2455	74
ϵ	2448	87
F	2443	97
ζ	2440	103
G	2438	108
η	2430	125
H	2417	151

been photographed by a vacuum spectrograph of Johann's type whose Rowland radius is 25 cm. The crystal is a quartz and the reflection of the first order of (110) plane is used. Photographs I, II and III show their photometer curves. The wave-lengths of the absorption maxima and minima and their energy separations from the edges are listed in Tables I, II and III. These data agree with Saur's¹³⁾ results.

§ 5. Conclusion

The calculated results are in fairly good agreements with experiments and they are

Table III. Wave-lengths and energy separations of absorption maxima and minima in the fine structure of titanium *K* absorption spectrum of anatase.

	Wave-length in x.u.	Energy separation in ev.
Edge	2490.9	
A	2489.0	3.8
α	2487.4	7.0
B	2481.7	18
β	2478.4	25
C	2474.9	32
γ	2465	53
D	2446	91
δ	2442	100
E	2437	110
ϵ	2432	120
F	2428	130
ζ	2421	143
G	2411	164

especially good in metals. Then, as it was already discussed in Report I, it is concluded that the present method and assumption, that the life time of the ejected electron is so short that the distant atoms from an absorbing atom of x-rays do not contribute to the absorption phenomena, are probable. Also, the free electron approach used in the calculation can be applied to metals but it is necessary to reconsider in the case of insulators.

In conclusion the author wishes to express his sincere thanks to Professor M. Sawada for his kind guidance and encouragement and to Professor T. Nagamiya for his kind comment and advice. The author also wishes to express his gratitude to Mr. T. Ishimura for his valuable discussion and his earnest assistance throughout the work and to Mr. T. Okano for his assistance in numerical calculation.

References

1) R. de L. Kronig: *Z. Phys.* **70** (1931) 317; **75** (1932) 191.

2) T. Hayasi: *Sci. Repts. Tohoku Univ. Ser. 1* **33** (1949) 123, 183; **34** (1950) 185. T. Hayasi and S. Okada: *Ibid. Ser. 1* **37** (1953) 331. A. I. Kostarev: *Zhur. Eksptl. Teoret. Fiz. S.S.S.R.* **11** (1941) 60; **19** (1941) 413; **21** (1951) 917.

3) T. Shiraiwa, T. Ishimura and M. Sawada: *J. Phys. Soc. Japan* **13** (1958) 847.

4) R. de L. Kronig: *Z. Phys.* **75** (1932) 468,

- H. Petersen: *Z. Phys.* **76** (1932) 768; **80** (1933) 258; **98** (1936) 569. D. R. Hartree, R. de L. Kronig and H. Petersen: *Physica* **1** (1934) 895. C. H. Shaw and T. M. Snyder: *Phys. Rev.* **58** (1940) 600. E. M. Corson: *Phys. Rev.* **70** (1946) 645.
- 5) N. F. Mott and H. S. W. Massey: *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1952).
- 6) R. E. Langer: *Phys. Rev.* **51** (1937) 669.
- 7) D. R. Hartree and W. Hartree: *Proc. Roy. Soc. A*, **157** (1936) 490.
- 8) K. Shibagaki: *The Numerical Solution of the Ordinary Differential Equations* (Iwanami, Tokyo, 1942) (in Japanese).
- 9) P. Löwdin and K. Appel: *Phys. Rev.* **103** (1956) 1746.
- 10) J. C. Slater: *Phys. Rev.* **36** (1930) 57.
- 11) W. Hartree, D. R. Hartree and B. Swirles: *Phil. Trans. Roy. Soc. A*, **238** (1939) 229.
- 12) F. Schossberger: *Z. Kris.* **104** (1942) 358. Von P. Ehlich: *Z. Elektroch.* **45** (1939) 362. M. L. Huggins: *Phys. Rev.* **27** (1926) 638.
- 13) E. Saur: *Ann. Physik* **42** (1942) 223.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

Studies on the Magnetic Anisotropy Induced by Cold Rolling of Ferromagnetic Crystal, II. Iron-Aluminum Alloys

By Sōshin CHIKAZUMI*, Kenzō SUZUKI** and Hiroko IWATA***

*Department of Physics and Chemistry, Gakushuin University,
Mejiro, Tokyo, Japan*

(Received September 12, 1959)

Magnetic anisotropy was measured on the several single crystals of Fe_3Al which were rolled in definite crystallographic directions. Rolling on (110) and parallel to [001] induced the uniaxial anisotropy as large as 7.1×10^5 erg/cc at only 12% reduction. The direction of easy magnetization in this case was parallel to roll direction, which was also confirmed by the observation of domain pattern. (110)[$\bar{1}\bar{1}0$], (001)[010] and (001)[110] rolling were also investigated.

Calculations were made on the roll magnetic anisotropy in terms of the "slip-induced directional order," under the assumption of $\{110\}\langle 111 \rangle$ slip system. It was found that dipole-dipole interaction between second nearest neighbors must be taken into consideration in order to explain the experimental facts.

§ 1. Introduction

It has been found that some alloys, for instance iron-nickel alloys, exhibit very strong anisotropy when they are rolled or cold-worked. This anisotropy, which is called as a roll magnetic anisotropy, has been utilized in the magnetic material "Isoperm" since the discovery of this phenomenon by Six, Snoek and Burgers¹⁾ in 1934. Several papers^{2), 3)}

have been published in connection with the origin of this anisotropy, but the phenomena were too complicated to be interpreted under a simple assumption such as the anisotropy due to internal stress and magnetostriction.

After the experiments using single crystal specimen of iron-nickel alloys, it was found by the present authors⁶⁾⁻⁸⁾ that the all experimental facts were satisfactorily explained in terms of slip-induced directional order rather than the mechanism proposed by Néel⁴⁾ and Taniguchi and Yamamoto⁵⁾. Almost the same interpretation was recently proposed by Bunge and Müller⁹⁾.

The aim of the present paper is to extend

* Present address: The Institute for Solid State Physics, The University of Tokyo, Azabu, Minato-ku, Tokyo.

** Present address: Central Laboratory, Riken Piston Ring Ind. Co. Ltd., Kumagaya, Saitama.

*** Present name: Mrs. Hiroko Wakiyama.

the investigation to the body-centered cubic crystal. Several single crystals of Fe_3Al were used as specimens, because this alloy has a low crystal anisotropy and a high value of magnetostriction (Cf. Fig. 1), which promised a high value of dipole-dipole interaction. Although comparatively large number of papers^{10,11)} have been published on the rolling of Fe-Al alloys in connection with the effort to get a grain-orientated material, no investigation was found as to the roll magnetic anisotropy of this alloy. The superstructure of Fe_3Al was well investigated by Bradly and Jay¹²⁾ by means of X-ray diffraction and also by Nathans, Pigott and Shull¹³⁾ by means of neutron diffraction together with the observation of its magnetic structure. These are the useful informations for the interpretation of the experimental results.

remove a skeleton structure and cooled in a furnace.

The specimens were first shaped into the rectangular plates, 3–8 mm in length and width, and 0.8–2.0 mm in thickness. Crystallographic orientation of the plates was (001) [010], (001) [110], (110) [001] and (110) [$\bar{1}\bar{1}$ 0] respectively. The alloy was so hard and brittle that it was not possible to roll down the crystal more than about 10%, which, however, was adequate to induce the roll magnetic anisotropy as large as several 10^6 erg/cc.

The domain patterns were observed on the rolled surface, side edge and top surface. The technique used was the same as used in the previous paper⁷⁾. The anisotropy was measured by means of torque magnetometer by using the specimens which were cut in a circular shape from the rolled single crystal plates. The size of the specimens were about 3.4–6.3 mm in diameter and 0.7–1.8 mm in thickness.

§ 3. Experimental Results

(1) (001) [010] rolling

Domain pattern observed on the rolled surface (Pl. 1) shows the domains separated by many 180° walls running in parallel to the roll direction. This means that the direction of easy magnetization is parallel to the roll direction. The observation on the top-surface (which is normal to the roll direction) reveals that easy direction is also parallel to the normal of the roll plane (Pl. 3). That means there is an plane of easy magnetization which is parallel to the side surface. Domains observed on the side surface direct in different way from place to place (Pl. 2).

The magnetic anisotropy energy measured by torque magnetometer can be expressed by

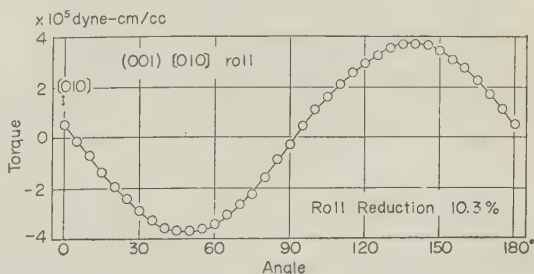


Fig. 2. Torque curve of rolled (001) [010] single crystal plate of Fe_3Al .

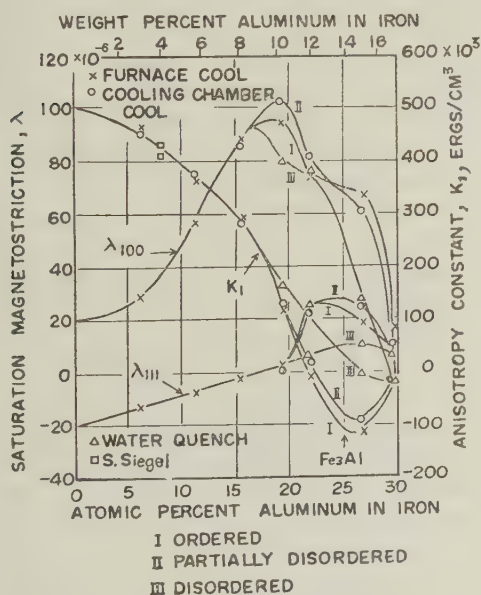


Fig. 1. Dependence of the coefficient of crystal anisotropy K_1 and that of magnetostriction λ_{100} , λ_{111} on the composition of Fe-Al alloys (after R. C. Hall: J. Appl. Phys. **28** (1957) 711, **30** (1959) 817).

§ 2. Specimens and Experimental Procedure

Specimens used were the single crystals of Fe_3Al which were made by solidifying from the melt in a high vacuum induction furnace. The raw materials used were 99.9% electrolytic iron and 99.997% aluminum. After cutting, the specimens were annealed for 3 hours at 1000° – 1200°C in a hydrogen atmosphere to

$$E=-K_u\cos^2(\theta-\theta_0), \tag{1}$$

where θ is the angle of inner magnetization measured from roll direction. The torque curve in this case is shown in Fig. 2, which can be well fitted by Eq. (1) with the values,

$$\left. \begin{aligned} K_u &= 3.70 \times 10^5 \text{ erg/cc for } r = 10.3\% \\ \theta_0 &= 0. \end{aligned} \right\} \tag{2}$$

(2) (001) [110] rolling

The domain patterns in this case are shown in Pls. 4, 5 and 6 for roll plane, side edge and top surface respectively. Although both roll plane and top surface show no distinct domain structure, but the side surface shows that the inner magnetization is perpendicular to the roll plane. The torque curve (Fig. 3) can be expressed by Eq. (1) with

$$\left. \begin{aligned} K_u &= 1.76 \times 10^5 \text{ erg/cc for } r = 10\% \\ \theta_0 &= 27^\circ. \end{aligned} \right\} \tag{3}$$

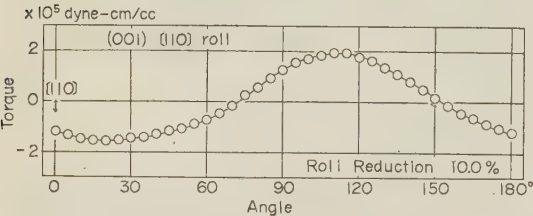


Fig. 3. Torque curve of rolled (001) [110] single crystal plate of Fe₃Al.

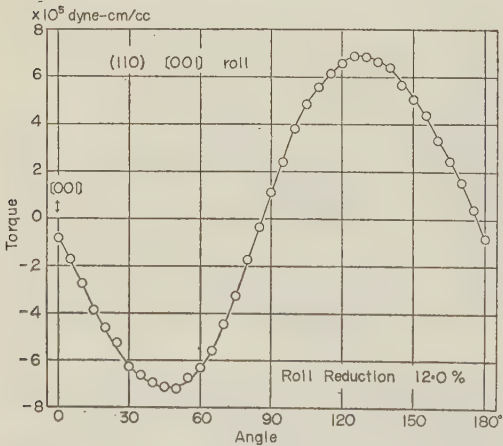


Fig. 4. Torque curve of rolled (110) [001] single crystal plate of Fe₃Al.

(3) (110) [001] rolling

The most distinct domain patterns were observed in this case, as shown in Pls. 7, 8 and 9. The domains are running in parallel to the roll direction as shown in Pls. 7 and

8. The patterns appearing on the top surface (Pl. 9) is to be called “maze pattern,” which is the evidence that the inner magnetization strikes the surface almost perpendicularly¹⁴.

The torque curve in this case (Fig. 4) can be expressed by Eq. (1) with

$$\left. \begin{aligned} K_u &= 7.06 \times 10^5 \text{ erg/cc at } r = 12\% \\ \theta_0 &= 0. \end{aligned} \right\} \tag{4}$$

(4) (110) [110] rolling

Domain patterns in this case of rolling are shown in Pls. 10, 11 and 12, which show the domains running perpendicularly to the roll direction in the plane of rolling. The crystallographic direction of inner magnetization in

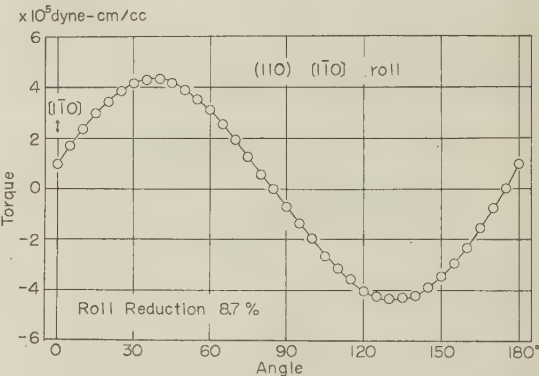


Fig. 5. Torque curve of rolled (110) [110] single crystal plate of Fe₃Al.

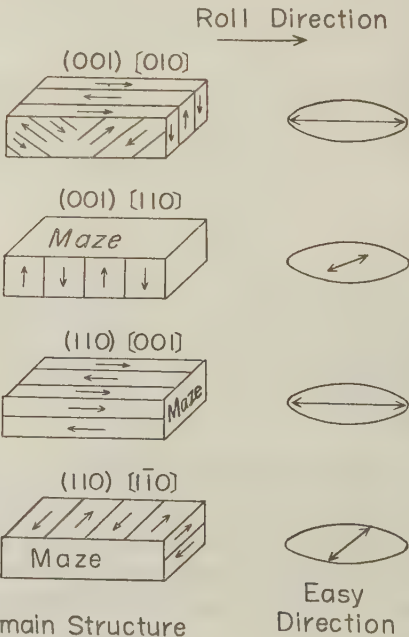


Fig. 6. Domain structures and the direction of easy magnetization in the plane of rolling.

this case is the same as in the case of (110) [001] rolling (See Fig. 6).

The torque curve (Fig. 5) can be fitted by Eq. (1) with

$$\left. \begin{aligned} K_u &= 4.34 \times 10^5 \text{ erg/cc for } r=8.7\% \\ \theta_0 &= \pi/2. \end{aligned} \right\} \quad (5)$$

The results of the domain pattern observation and the direction of easy magnetization determined by torque measurement are summarized in Fig. 6. The values of K_u are also tabulated in Tab. II.

§ 4. Mechanism of Inducing Magnetic Anisotropy by Slip Deformation

It has been reported that the slip planes which contribute to the deformation of body-centered cubic crystal are $\{110\}$, $\{112\}$ and $\{123\}^{15}$. In the present crystal, however, it was found after a close examination of slip bands (Cf. Pls. 2, 3, 5, 6, 8 and 12), that almost all deformations are attained by the slip systems which belong to $\{110\} \langle 111 \rangle$. We shall assume, therefore, that all deformations are exclusively produced by $\{110\} \langle 111 \rangle$ slip systems.

Next we shall deal with the unbalanced distribution of atom pairs induced by slip deformation. When the slip takes place in a somewhat ordered crystal, the ordered atom pairs which connect the both sides of the slipped plane are destroyed, while the ordered atom pairs which lie in the slipped plane are maintained. Thus the slips induce the unbalanced distribution of ordered atom pairs. Then the dipole-dipole interaction between neighboring atoms, which usually does not give rise to any anisotropy energy, induces the uniaxial anisotropy energy given by

$$E = l \sum_i N_{BBi} \cos^2 \varphi_i, \quad (6)$$

where N_{BB} is the number of BB pairs which direct in i -th pair direction, φ_i is the angle between magnetization and i -th pair direction and l is given by

$$l = l_{AA} + l_{BB} - 2l_{AB}, \quad (7)$$

where l_{AA} , l_{BB} and l_{AB} are the coefficients of dipole-dipole interaction of AA, BB and AB atom pairs (Cf. Ref. 7)). Thus in order to calculate the roll magnetic anisotropy, we must first calculate the distribution of B-B (or Al-Al) pairs resulting from slip deformation.

Now it should be pointed out that the atom

pairs connecting the first nearest neighboring atoms are the second importance in the present case. This is because the directions of the first nearest neighbor pairs are $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}11]$ and $[\bar{1}\bar{1}1]$, two of which lie in the slip plane, while the other two are out of the slip plane. If, therefore, the slips take place along the two slip planes which intersect perpendicularly with each other, the four kinds of atom pairs are equally destroyed, thus resulting no magnetic anisotropy. This may be the case for the rolling of the crystal having high symmetrical crystallographic orientation such as used in the present investigation.

Then the dipole-dipole interaction between the second nearest neighboring atoms must be taken into consideration. According to the experiment of magnetic annealing made by one of the authors on Fe_3Al crystal¹⁶, it is concluded that the dipole-dipole interaction between the second nearest neighbors is appreciably large as well as between the first nearest neighbors.

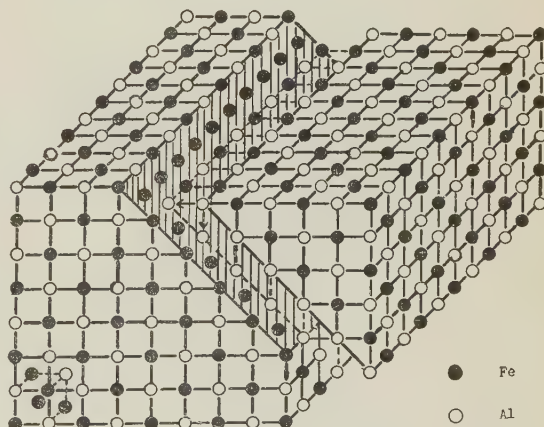


Fig. 7. Directional order induced by the slip occurred in the ordered Fe_3Al crystal.

Now let us suppose the perfectly ordered Fe_3Al crystal in which two dislocations passed through (011) plane and in the direction $[1\bar{1}\bar{1}]$ (Fig. 7). The bond directions of second neighbor pairs are $[100]$, $[010]$ and $[001]$. In this case the atom pairs which direct to $[100]$ lie in the slipped plane and therefore remain unchanged, whereas the other two which direct to $[010]$ and $[001]$ must be altered into more disordered pairs.

Now we shall calculate the number of BB

pairs appearing during deformation. In the A_3B type ordered crystal, in which the degree of short range order is given by σ , the number of BB pairs which direct to $[100]$ is calculated to be $\sqrt{2}(1-\sigma)/16a^2$ per unit area of (011) plane, where a is the lattice constant. In the case of the disordered state it should become $\sqrt{2}/16a^2$. It is concluded, therefore, that the slip deformation as shown in Fig. 7 makes the number of BB pairs which direct to $[100]$ less than the others by $\sqrt{2}\sigma/16a^2$ per unit area of (011) .

Let us suppose the ns dislocations run through the n atomic planes, where s is to be called as "slip density." Since the number of dislocations per unit depth of the crystal which was measured along the normal of the slip plane is given by $\sqrt{2}s/a$, the difference of the number of BB pairs per unit volume between $[100]$ and others will be given by

$$\begin{aligned} \Delta N_{BB} &= -\frac{\sqrt{2}\sigma}{16a^2} \times \frac{\sqrt{2}s}{a} \times \frac{p}{4} \\ &= -\frac{p\sigma}{32a^3} s \\ &= -\frac{p\sigma N}{64} s, \end{aligned} \quad (8)$$

where p is the probability that a dislocation results in a disordered slipped plane (Cf. Eq. (2) in Ref. 7)) and N is the number of atoms per unit volume. Putting (8) into (6), we have the anisotropy energy

$$E = -\frac{p\sigma N l_2}{64} |s_i| \alpha_i^2, \quad (9)$$

where l_2 means l of the second nearest neighbor pairs. Eq. (9) is also valid for $(011)[1\bar{1}1]$, $(01\bar{1})[111]$ and $(0\bar{1}1)[111]$ slip systems. Generally, we can express the anisotropy as

$$E = -\frac{p\sigma N l_2}{64} \sum_i |s_i| f_i(\alpha_1, \alpha_2, \alpha_3), \quad (10)$$

where

$$f_i(\alpha_1, \alpha_2, \alpha_3) = \alpha_1^2 \beta_1 + \alpha_2^2 \beta_2 + \alpha_3^2 \beta_3. \quad (11)$$

$(\beta_1, \beta_2, \beta_3)$ in this equation means the direction cosines of $\langle 100 \rangle$ direction which lies in the slip plane of the i -th slip system. The coefficients of α_i^2 in (10) are tabulated in Tab. I, together with the strain tensors for all slip systems.

It should be noticed that in the case of the body-centered cubic crystal, there is no need to classify the anisotropy into L.F. and S.C. types, as in the case of the face-centered cubic crystal (Cf. Ref. 7)), because in this case the slip plane contains only one sort of atom-pair direction and in any case the induced anisotropy can be written by the number of BB pairs which direct in this direction.

§5. Calculation of the Slip Deformation

In this section, we shall calculate the slip density s_i of each slip system for every cases of rolling. When the slip deformation takes place in one of the slip systems, say $(011)[1\bar{1}1]$ ($i=2$) as shown in Fig. 7, the deformation of the crystal can be expressed by the strain tensor, each component of which is given by

Tab. I. Strain tensors and the coefficients in $f_i(\alpha_1, \alpha_2, \alpha_3)$ (Cf. Eq. (11)) for each slip system.

No. of slip system	Slip plane	Slip direction	Component of strain tensor						Coefficients in $f_i(\alpha_k)$		
			γ_{xx}	γ_{yy}	γ_{zz}	γ_{yz}	γ_{zx}	γ_{xy}	α_1^2	α_2^2	α_3^2
1	(011)	$[1\bar{1}1]$	0	s_1	$-s_1$	0	$\frac{1}{2}s_1$	$\frac{1}{2}s_1$	1	0	0
2		$[1\bar{1}\bar{1}]$	0	s_2	$-s_2$	0	$-\frac{1}{2}s_2$	$-\frac{1}{2}s_2$	1	0	0
3	(01 $\bar{1}$)	$[111]$	0	s_3	$-s_3$	0	$-\frac{1}{2}s_3$	$\frac{1}{2}s_3$	1	0	0
4		$[\bar{1}11]$	0	s_4	$-s_4$	0	$\frac{1}{2}s_4$	$-\frac{1}{2}s_4$	1	0	0
5	(101)	$[1\bar{1}\bar{1}]$	s_5	0	$-s_5$	$\frac{1}{2}s_5$	0	$\frac{1}{2}s_5$	0	1	0
6		$[\bar{1}11]$	s_6	0	$-s_6$	$-\frac{1}{2}s_6$	0	$-\frac{1}{2}s_6$	0	1	0
7	(10 $\bar{1}$)	$[111]$	s_7	0	$-s_7$	$-\frac{1}{2}s_7$	0	$\frac{1}{2}s_7$	0	1	0
8		$[1\bar{1}\bar{1}]$	s_8	0	$-s_8$	$\frac{1}{2}s_8$	0	$-\frac{1}{2}s_8$	0	1	0
9	(110)	$[1\bar{1}\bar{1}]$	$-s_9$	s_9	0	$-\frac{1}{2}s_9$	$-\frac{1}{2}s_9$	0	0	0	1
10		$[\bar{1}11]$	$-s_{10}$	s_{10}	0	$\frac{1}{2}s_{10}$	$\frac{1}{2}s_{10}$	0	0	0	1
11	(1 $\bar{1}$ 0)	$[111]$	$-s_{11}$	s_{11}	0	$\frac{1}{2}s_{11}$	$-\frac{1}{2}s_{11}$	0	0	0	1
12		$[1\bar{1}\bar{1}]$	$-s_{12}$	s_{12}	0	$-\frac{1}{2}s_{12}$	$\frac{1}{2}s_{12}$	0	0	0	1

$$\left. \begin{aligned} \gamma_{xx2}=0, \quad \gamma_{yy2}=S_2, \quad \gamma_{zz2}=-S_2, \\ \gamma_{yz2}=0, \quad \gamma_{xz2}=-\frac{1}{2}S_2, \quad \gamma_{xy2}=\frac{1}{2}S_2. \end{aligned} \right\} \quad (12)$$

The components of the strain tensors for all slip systems are summarized in Tab. I. As a result of the contribution of several slip systems, the actual deformation of the crystal can be expressed by

$$\left. \begin{aligned} \gamma_{xx}=\sum_i \gamma_{xxi}, \quad \gamma_{yy}=\sum_i \gamma_{yyi}, \quad \gamma_{zz}=\sum_i \gamma_{zz i}, \\ \gamma_{yz}=\sum_i \gamma_{yzi}, \quad \gamma_{xz}=\sum_i \gamma_{xzi}, \quad \gamma_{xy}=\sum_i \gamma_{xyi}. \end{aligned} \right\} \quad (13)$$

(1) (001) [010] rolling

It is assumed as was in the previous paper⁷⁾ that the rolling in this case results in an elongation in length and a reduction in width but no widening of the specimen. Then the deformation of the crystal in this case should be given by

$$\left. \begin{aligned} \gamma_{xx}=0, \quad \gamma_{yy}=2r, \quad \gamma_{zz}=-2r, \\ \gamma_{yz}=0, \quad \gamma_{xz}=0, \quad \gamma_{xy}=0, \end{aligned} \right\} \quad (14)$$

where r is the reduction of the thickness.

(001) [010] roll

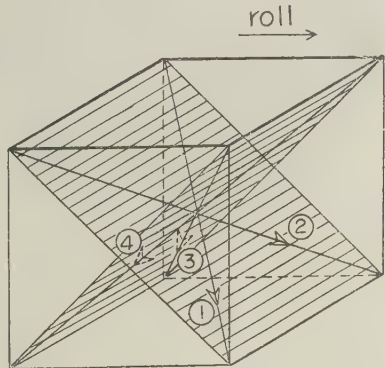


Fig. 8. Effective slip systems in the case of (001) [010] rolling.

It may be reasonable to assume that the slip systems which is effective in this case are $i=1, 2, 3$ and 4 as shown in Fig. 8, for the other slip systems must result in a finite value of γ_{xx} , γ_{yz} , γ_{xz} or γ_{xy} . Then Eq. (13) becomes

$$\left. \begin{aligned} \gamma_{xx}=0, \\ \gamma_{yy}=S_1+S_2+S_3+S_4, \\ \gamma_{zz}=-(S_1+S_2+S_3+S_4), \\ \gamma_{yz}=0, \\ \gamma_{xz}=\frac{1}{2}(S_1-S_2-S_3+S_4), \\ \gamma_{xy}=\frac{1}{2}(S_1-S_2+S_3-S_4). \end{aligned} \right\} \quad (15)$$

Comparing (15) with (14), we have

$$\left. \begin{aligned} S_1+S_2+S_3+S_4=2r, \\ S_1=S_2, \\ S_3=S_4. \end{aligned} \right\} \quad (16)$$

(2) (001) [110] rolling

The deformation of the crystal in this case should be given by

$$\left. \begin{aligned} \gamma_{xx}=r, \quad \gamma_{yy}=r, \quad \gamma_{zz}=-2r, \\ \gamma_{yz}=0, \quad \gamma_{xz}=0, \quad \gamma_{xy}=r. \end{aligned} \right\} \quad (17)$$

The effective slip systems in this deformation would be $i=1, 3, 5$ and 7 (Fig. 9). Then Eq. (13) becomes

$$\left. \begin{aligned} \gamma_{xx}=S_5+S_7, \\ \gamma_{yy}=S_1+S_3, \\ \gamma_{zz}=-(S_1+S_3+S_5+S_7), \\ \gamma_{yz}=\frac{1}{2}(S_5-S_7), \\ \gamma_{xz}=\frac{1}{2}(S_1-S_3), \\ \gamma_{xy}=\frac{1}{2}(S_1+S_3+S_5+S_7). \end{aligned} \right\} \quad (18)$$

(001) [110] roll

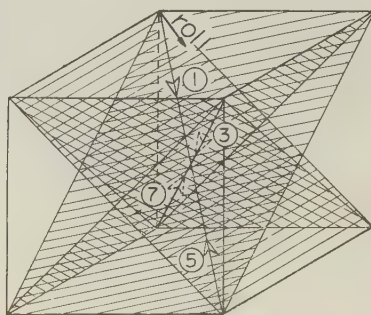


Fig. 9. Effective slip systems in the case of (001) [110] rolling.

(110) [001] roll

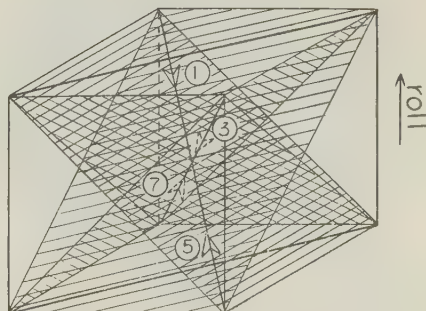


Fig. 10. Effective slip systems in the case of (110) [001] rolling.

Comparing (18) with (17), we have

$$s_1 = s_3 = s_5 = s_7 = \frac{r}{2}. \quad (19)$$

(3) (110) [001] rolling

The deformation in this case should be

$$\left. \begin{aligned} \gamma_{xx} &= -r, & \gamma_{yy} &= -r, & \gamma_{zz} &= 2r, \\ \gamma_{yz} &= 0, & \gamma_{zx} &= 0, & \gamma_{xy} &= -r. \end{aligned} \right\} \quad (20)$$

The effective slip systems in this case are $i=1, 3, 5$ and 7 (Fig. 10), which are the same as in the case of (001) [110] rolling. Eq. (13), therefore, should be given by (18). Comparing (18) with (20), we have

$$s_1 = s_3 = s_5 = s_7 = -\frac{r}{2}. \quad (21)$$

(4) (110) [$\bar{1}\bar{1}$ 0] rolling

The rolling in this case resulted in not only elongation and thinning but also widening of the crystal. This is supposedly because the most easily glidable slip systems $i=1, 3, 5$ and 7 must contribute to the widening of the crystal. The actual deformation of the crystal was 3.8% in elongation, 4.2% in widening and 8.7% in a reduction of the thickness. Then we shall simply assume the elongation, widening and a reduction of the thickness to be $r/2$, $r/2$ and $-r$ respectively. Thus we have

$$\left. \begin{aligned} \gamma_{xx} &= -\frac{1}{2}r, & \gamma_{yy} &= -\frac{1}{2}r, & \gamma_{zz} &= \frac{1}{2}r, \\ \gamma_{yz} &= 0, & \gamma_{zx} &= 0, & \gamma_{xy} &= -\frac{3}{2}r. \end{aligned} \right\} \quad (22)$$

In this case we have to assume the occurrence of the slips in the systems $i=1, 3, 5, 7; 2, 4, 6$ and 8 (Fig. 11). From the symmetry consideration, we shall assume

(110) [$\bar{1}\bar{1}$ 0] roll

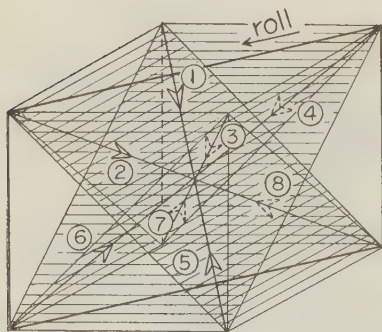


Fig. 11. Effective slip systems in the case of (110) [$\bar{1}\bar{1}$ 0] rolling.

$$\left. \begin{aligned} s_1 &= s_3 = s_5 = s_7 = s, \\ s_2 &= s_4 = s_6 = s_8 = s'. \end{aligned} \right\} \quad (23)$$

Then Eq. (13) becomes

$$\left. \begin{aligned} \gamma_{xx} &= 2(s + s'), \\ \gamma_{yy} &= 2(s + s'), \\ \gamma_{zz} &= -4(s + s'), \\ \gamma_{yz} &= 0, \\ \gamma_{zx} &= 0, \\ \gamma_{xy} &= 2(s - s'). \end{aligned} \right\} \quad (24)$$

Comparing (24) with (22), we have

$$\left. \begin{aligned} s &= -\frac{1}{4}r, \\ s' &= \frac{1}{8}r. \end{aligned} \right\} \quad (25)$$

§ 6. Calculation of Magnetic Anisotropy and its Comparison with Experiment

By putting the values of s_i obtained in the previous section into (10), we can get the expression of the anisotropy energy. We shall calculate it below for each case of rolling and compare it with experimental results.

(1) (001) [010] rolling

Putting (16) into (10), we have

$$\begin{aligned} E &= -\frac{p\sigma N l_2}{64} (s_1 + s_2 + s_3 + s_4) \alpha_1^2 \\ &= -\frac{p\sigma N l_2}{32} r \alpha_1^2. \end{aligned} \quad (26)$$

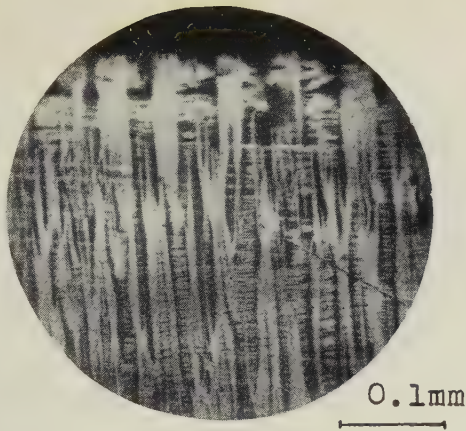
This means that [100] is the direction of hard magnetization, in other words (100) plane is the plane of easy magnetization, provided $l_2 < 0$. This is the case as illustrated in Fig. 6. The directions of magnetization in the plane of easy magnetization (Cf. Pl. 2) are possibly determined by the anisotropy of the first neighbor directional order which is induced by the unbalanced occurrence of the slips among the paired slip systems. When the magnetization is restricted in (001) plane, as in the case for torque measurement, (26) becomes

$$E = \frac{p\sigma N l_2}{32} r \cos^2 \theta, \quad (27)$$

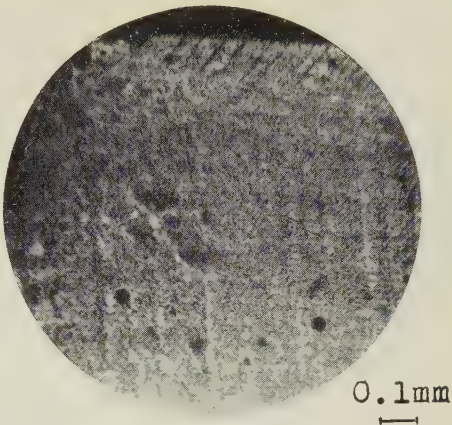
where θ is the angle of magnetization measured from roll direction. Comparing (27) with (1), we have

$$\left. \begin{aligned} K_u &= -\frac{p\sigma N l_2}{32} r, \\ \theta_0 &= 0. \end{aligned} \right\} \quad (28)$$

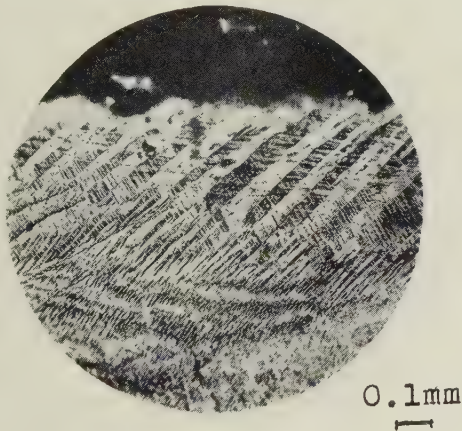
Comparing it with experimental result (2), we have



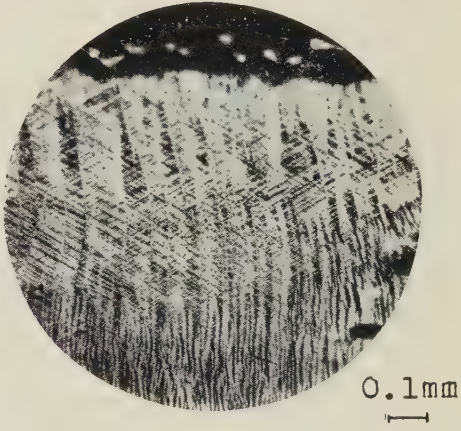
Pl. 1. Roll plane, (001) [010] rolling ($r=6.7\%$)



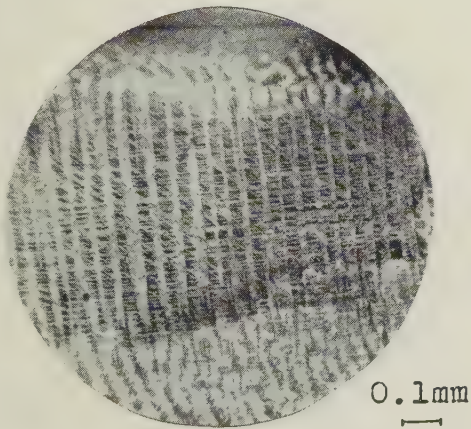
Pl. 4. Roll plane, (001) [110] rolling ($r=15\%$)



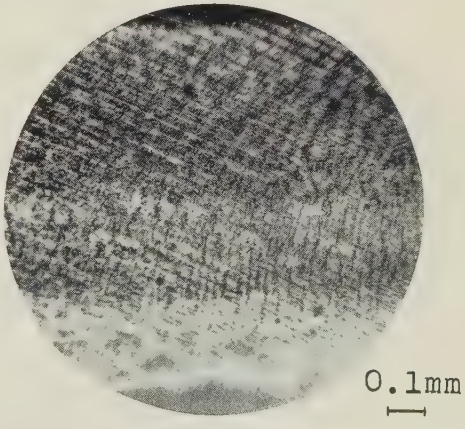
Pl. 2. Side edge, (001) [010] rolling ($r=6.7\%$)



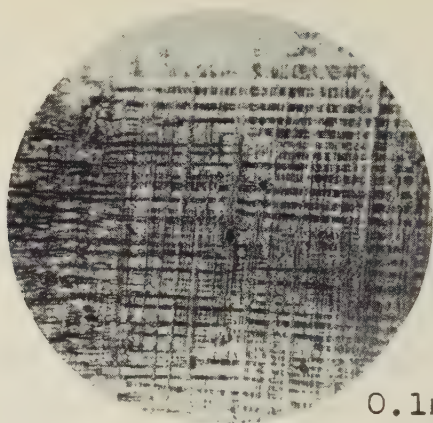
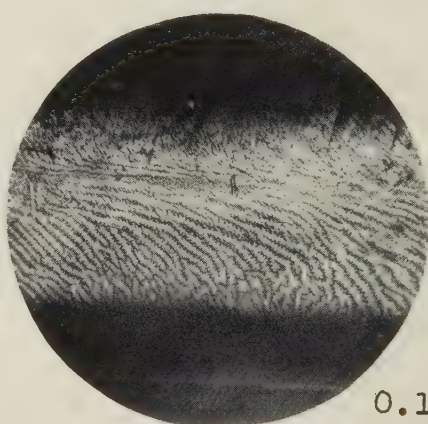
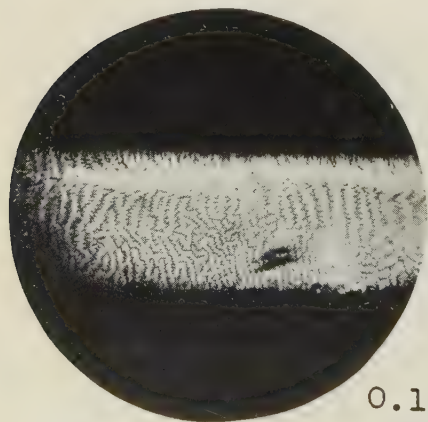
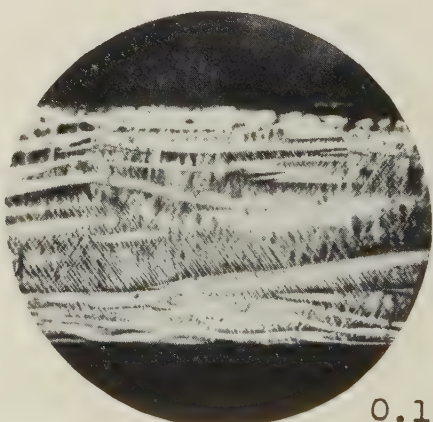
Pl. 5. Side edge, (001) [110] rolling ($r=15\%$)



Pl. 3. Top surface, (001) [010] rolling ($r=6.7\%$)



Pl. 6. Top surface, (001) [110] rolling ($r=15\%$)

Pl. 7. Roll plane, (110) [001] rolling ($r=10\%$)Pl. 10. Roll plane, (110) $[1\bar{1}0]$ rolling ($r=10\%$)Pl. 8. Side edge, (110) [001] rolling ($r=10\%$)Pl. 11. Side edge, (110) $[1\bar{1}0]$ rolling ($r=10\%$)Pl. 9. Top surface, (110) [001] rolling ($r=10\%$)Pl. 12. Top surface, (110) $[1\bar{1}0]$ rolling ($r=10\%$)

$$p\sigma Nl_2 = -1.15 \times 10^8 \text{ erg/cc} . \quad (29)$$

(2) (001) [110] rolling

Putting (19) into (10), we have

$$\begin{aligned} E &= -\frac{p\sigma Nl_2}{64} \{(|s_1| + |s_3|)\alpha_1^2 + (|s_5| + |s_7|)\alpha_2^2\} \\ &= -\frac{p\sigma Nl_2}{64} r(\alpha_1^2 + \alpha_2^2) \\ &= \text{const.} + \frac{p\sigma Nl_2}{64} r\alpha_3^2 . \end{aligned} \quad (30)$$

This means that the direction of easy magnetization is parallel to [001], i.e. the normal of the roll plane. This is in good agreement with the experiment as illustrated in Fig. 6. When the magnetization is confined in the roll plane, however, (30) becomes

$$E = \text{const.} , \quad (31)$$

and therefore

$$K_u = 0 . \quad (32)$$

The experiment shows, however, the presence of a finite anisotropy energy as given in (3). The possible origin of this anisotropy may be considered to be either due to the rotation of the crystal by the unbalanced occurrence of the slips in the several slip systems or due to the appearance of the first neighbor BB pairs by the unbalanced occurrence of the paired slip systems.

(3) (110) [001] rolling

Putting (21) into (10), we have

$$\begin{aligned} E &= -\frac{p\sigma Nl_2}{64} \{(|s_1| + |s_3|)\alpha_1^2 + (|s_5| + |s_7|)\alpha_2^2\} \\ &= -\frac{p\sigma Nl_2}{64} r(\alpha_1^2 + \alpha_2^2) \\ &= \text{const.} + \frac{p\sigma Nl_2}{64} r\alpha_3^2 . \end{aligned} \quad (32)$$

Although this expression of the anisotropy is the same as in the case of (001) [110] rolling, it makes in this case the direction of easy magnetization parallel to the roll direction. This is in good agreement with the experiment illustrated in Fig. 6. When the magnetization is in (110), (32) becomes

$$E = \frac{p\sigma Nl_2}{64} r \cos^2 \theta , \quad (33)$$

hence we have

$$\left. \begin{aligned} K_u &= -\frac{p\sigma Nl_2}{64} r , \\ \theta_0 &= 0 . \end{aligned} \right\} \quad (34)$$

Comparing (34) with (4), we have

$$p\sigma Nl_2 = -3.76 \times 10^8 \text{ erg/cc} . \quad (35)$$

(4) (110) [110] rolling

Putting (23) and (25) into (10), we have

$$\begin{aligned} E &= -\frac{p\sigma Nl_2}{64} \{(|s_1| + |s_2| + |s_3| + |s_4|)\alpha_1^2 \\ &\quad + (|s_5| + |s_6| + |s_7| + |s_8|)\alpha_2^2\} \\ &= -\frac{3p\sigma Nl_2}{256} r(\alpha_1^2 + \alpha_2^2) \\ &= \text{const.} + \frac{3p\sigma Nl_2}{256} r\alpha_3^2 . \end{aligned} \quad (36)$$

This means that the easy direction is [001], i.e. perpendicular to the side surface. This is also the case as shown in Fig. 6. In the roll plane the anisotropy becomes

$$E = \frac{3p\sigma Nl_2}{256} r \cos^2 (\theta - \pi/2) , \quad (37)$$

hence we have

$$\left. \begin{aligned} K_u &= \frac{3p\sigma Nl_2}{256} r , \\ \theta_0 &= \pi/2 . \end{aligned} \right\} \quad (38)$$

Tab. II. Comparison between experimental value of the coefficient of roll magnetic anisotropy and calculation.

Roll plane	Roll direction	Observed		Calculation K_u	Value of $P\sigma Nl_2$ erg/cc
		K_u erg/cc	Easy direction		
(001)	[010]	3.70×10^6 $r=10.3\%$	[010]	$-\frac{p\sigma Nl_2}{32}r$	-1.15×10^8
	[110]	1.76×10^6 $r=10\%$	27° from roll direction	0	—
(110)	[001]	7.06×10^6 $r=12\%$	[001]	$-\frac{p\sigma Nl_2}{64}r$	-3.76×10^8
	[110]	-4.34×10^6 $r=8.7\%$	[001]	$\frac{3p\sigma Nl_2}{256}r$	-4.25×10^8

Comparing it with the experiment (5), we have

$$p\sigma NI_2 = -4.25 \times 10^8 \text{ erg/cc.} \quad (39)$$

§ 7. Conclusion and Discussion

As mentioned above, the theory well explained the direction of easy magnetization or the orientation of easy magnetization plane for every cases of rolling. The quantitative results are summarized in Tab. II. The values of $p\sigma NI_2$ obtained for each case of rolling is in fairly good agreement with one another. The slight difference in the value between the cases of (001) and (110) roll planes would be caused by some difference in the condition of slip deformation.

Now let us discuss about the magnitude of $p\sigma NI_2$. As was done by Néel¹⁷⁾ as to the magnetic annealing, the value of NI (Cf. (7)) can be obtained by analyzing the dependence of the magnetostriction constants λ_{100} and λ_{111} on the alloy composition. In the present case the situation is somewhat complicated, because the two kinds of atom-pairs, i.e. the first and second neighbor pairs, must be taken into consideration. Fortunately, however, we have the information that ratio of the dipole-dipole interaction of the first neighbor pair to the second neighbor pair is $l_1:l_2=1.35:1$, which was concluded by one of the authors¹⁰⁾ from the experiment of magnetic annealing made on the single crystal of Fe_3Al . Comparing the theory, which assumes the above-mentioned ratio of the dipole-dipole coupling, with the curves of λ_{100} and λ_{111} given in Fig. 1, we have the value

$$\begin{aligned} NI_2 &= N(l_{2\text{FeFe}} + l_{2\text{AlAl}} - 2l_{2\text{FeAl}}) \\ &= -30.1 \times 10^8 \text{ erg/cc.} \end{aligned} \quad (40)$$

The sign is in agreement to that assumed in § 6. From the mean value $p\sigma NI_2 = -4 \times 10^8$ for (110) roll plane and the value given in (40), we have

$$p\sigma = 13.3\% . \quad (41)$$

It is interesting that this value is considerably larger than that of Ni_3Fe , i.e. pS^2 or $p'\sigma = 1.6 \sim 5.9\%$ which was concluded in the previous paper⁷⁾. Since the degree of order σ or S is

supposedly not so different between Fe_3Al and Ni_3Fe , the difference in the value $p\sigma$ would be caused by the difference in the value of p .

It would be plausible to suppose that the dislocations in the ordered Fe_3Al crystal can not easily make pairs, because in this case four dislocations are necessary to recover the ordered arrangement between the both sides of the slipped plane, whereas it can be attained by only two dislocations for the ordered Ni_3Fe crystal. It would be interesting to examine such behavior of dislocation in the body-centered cubic crystal, but unfortunately the authors can not find out such investigation which was made on the basis of the dislocation theory.

References

- 1) W. Six, J. L. Snoek and W. G. Burgers: *De Ingenier* **49** (1934) E 195.
- 2) H. W. Conradt, O. Dahl and K. J. Sixtus: *Z. Metallkunde* **32** (1940) 231.
- 3) G. W. Rathenau and J. L. Snoek: *Physica* **8** (1941) 555.
- 4) L. Néel: *Compt. rend.* **238** (1954) 305; *J. phys. radium* **15** (1954) 225.
- 5) S. Taniguchi and M. Yamamoto: *Sci. Repts. Res. Inst. Tohoku Univ.* **A6** (1954) 330.
- 6) S. Chikazumi and K. Suzuki: *Phys. Rev.* **98** (1955) 1130.
- 7) S. Chikazumi, K. Suzuki and H. Iwata: *J. Phys. Soc. Japan* **12** (1957) 1259.
- 8) S. Chikazumi: *J. Appl. Phys.* **29** (1958) 346.
- 9) H. J. Bunge and H. G. Müller: *Wiss. Zeit. dech Hochschule für Verk. Dresden* **5** (1957) 327; H. J. Bunge: *Z. Metallkunde* **49** (1958) 40.
- 10) R. M. Bozorth, H. J. Williams and R. J. Morris: *Phys. Rev.* **58** (1940) 217.
- 11) D. Pavlovic and K. Foster: *J. Appl. Phys.* **29** (1958) 368.
- 12) A. J. Bradley and A. H. Jay: *Proc. Roy. Soc.* **A136** (1932) 210.
- 13) R. Nathans, M. T. Pigott and C. G. Shull: *J. Phys. Chem. Solid* **6** (1958) 38.
- 14) S. Chikazumi and K. Suzuki: *J. Phys. Soc. Japan* **10** (1955) 523.
- 15) for instance Cf. C. S. Barrett: *Structure of Metals* (McGraw-Hill Book Co., 1943).
- 16) K. Suzuki: *J. Phys. Soc. Japan* **13** (1958) 756.
- 17) L. Néel: *J. phys. radium* **15** (1954) 225.

Dielectric Relaxation in High Polymers, II. Vinylc High Polymers

By Tomoyasu TANAKA

*Department of Physics, Faculty of Science,
Kyusyu University, Hukuoka*

and Yōichi ISHIDA

*Department of Applied Chemistry, Faculty of Engineering,
Kyusyu University, Hukuoka, Japan*

(Received October 7, 1959)

In vinylc high polymers, there are two absorption mechanisms, one is at high temperatures and the other at low temperatures. From a general consideration, it is possible to separate the motion of high polymer molecule into two distinct modes, rotation and vibration. The high temperature absorption is attributed to the rotational relaxation and the low temperature absorption to the vibrational relaxation. A formal relation is obtained which connects the low temperature absorption curve to the vibrational frequency spectrum.

§ 1. Introduction

In the preceding paper¹⁾ a detailed description was given of the experimental data on the dielectric absorptions in high polymers at high as well as at low temperatures. The behaviors of these absorptions were summarized in three characteristics. For the high temperature absorption (α -absorption). (α -1) The shape of the absorption curve at constant temperature is approximately of the Debye type above a certain temperature and the shape changes only slightly with temperature. But at very low temperature the shape becomes very flat and the absorption seems to disappear. (α -2) The frequency at which the absorption reaches its maximum moves very rapidly with temperature, i.e. the apparent activation energy has a big value. (α -3) The absolute magnitude of the absorption peak depends strongly on the molecular structure of high polymers. The characteristics of the low temperature absorption (β -absorption) are rather different from those of the α -absorption. (β -1) The shape of the absorption curve is very broad at lower temperatures, and it becomes narrower with increasing temperature. (β -2) The frequency of maximum absorption changes very slowly with temperature, i.e. the apparent activation energy is relatively small. (β -3) The absolute magnitude of β -absorption is very small irrespective of the molecular structure of high polymers, i.e. the value is almost constant for all dipolar high

vinylc polymers.

We also proposed the following mechanisms which describe the dielectric behavior phenomenologically. The α -absorption is due to the transition of dipoles from one equilibrium configuration to another, and the β -absorption is due to the displacement of equilibrium positions of dipoles by the applied field.

In § 2 of this paper we shall discuss why the motion of dipoles is decomposed into two distinct modes, of which the one is effective for the α -absorption and the other is responsible for the β -absorption. In § 3 a qualitative discussion is given which shows that the frequency spectrum of molecular vibration about an equilibrium configuration consists of two branches. It is well known that in a periodic structure in which the light atoms and the heavy atoms alternate periodically, the spectrum of molecular vibration splits into optical and acoustical branches. In the same way, in a molecule of dipolar high polymer the dipolar groups are arranged periodically along the carbon chain irrespective of their isotactic, syndiotactic or atactic arrangement. The frequency spectrum of molecular vibrations would, therefore, split into two branches, although the distinction between optical and acoustical branches may not be clear because of a disordered orientation of carbon chain and an additional interaction between molecules in high polymers. In § 4 the distribution function of molecular motion is discussed

on the basis of the analysis given in the preceding sections. It is shown that the distribution function can be decomposed into configurational and vibrational parts. The former specifies the probability of finding the system in various local equilibrium configurations of dipolar groups and the latter specifies the vibrational state of molecules about a specific equilibrium configurations. Then it is shown that at low temperatures the transition between various local equilibrium configurations is frozen because of the high value of the pertinent activation energy compared with the thermal energy, and that only the transitions between vibrational states takes place. This is the mechanism by which we can interpret the characteristics of the low temperature β -absorption. It is very difficult to calculate the frequency spectrum from the knowledge of molecular structure. In § 5 a formal relation between the complex dielectric constant and the frequency spectrum is obtained. Since it is known that there are two corresponding absorptions in the visco-elastic properties of high polymers, the mechanism proposed in this paper should be applied to the interpretation of the properties, but a detailed discussion will be a subject of further investigation.

§ 2. Hamiltonian of the High Polymer Molecules*

For the sake of simplicity we shall consider only the simplest vinylic high polymers $(\text{CH}_2-\text{CHX})_n$ such as polyvinyl chloride. Let the number of electronegative atoms (the chlorine atoms in polyvinyl chloride) be $N=N_0n$, where N_0 is the number of molecules in the system, then the number of carbon atoms is just $2N=2N_0n$. We shall attach an effective charge $-e^*$ to each chlorine atom and $+e^*$ to each corresponding carbon atom so as to construct a dipole of appropriate magnitude for each C-X bond. The number of hydrogen atoms is three times as much as that of chlorine atoms.

* Since our treatment in this section is of entirely formal and phenomenological one, we can describe the physical conditions of high polymers without using any mathematical expressions. But the mathematical expressions tell us more about the underlying physical ideas and will be helpful when we formulate molecular theories.

The kinetic energy of the system is given by

$$T = (M_0/2) \sum_{(j=1, \dots, 2N; \lambda=1, 2, 3)} \dot{S}_{j,\lambda}^2, \quad (2.1)$$

where M_0 is the mass of carbon atom and the vectors $S_{j,\lambda}$'s are defined by

$$\left. \begin{aligned} S_{2j-1,1} &= r_{2j-1}, \\ S_{2j-1,\lambda} &= (m/M_0)^{1/2} r_{2j-1,\lambda}, \quad \lambda=2, 3, \end{aligned} \right\} \quad (2.2)$$

$$\left. \begin{aligned} S_{2j,1} &= r_{2j}, \\ S_{2j,2} &= (M/M_0)^{1/2} R_{2j}, \\ S_{2j,3} &= (m/M_0)^{1/2} r_{2j,3}, \end{aligned} \right\} \quad (2.3)$$

where r_{2j-1} , r_{2j} are the coordinates of carbon atoms in the j -th monomer unit, R_{2j} is the coordinate of chlorine atom, and $r_{2j-1,2}$, $r_{2j-1,3}$, $r_{2j,3}$ are the coordinates of hydrogen atoms, and M_0 , M , m are the masses of carbon, chlorine and hydrogen atoms respectively. The potential energy of the total system is given by

$$V = V_0(S_{j,\lambda}) + V_F(S_{j,\lambda}), \quad (2.4)$$

where $V_0(S_{j,\lambda})$ is the potential energy in the absence of the external electric field and $V_F(S_{j,\lambda})$ is the potential energy due to the applied field. The functional dependence of $V_0(S_{j,\lambda})$ on $S_{j,\lambda}$'s is rather complicated because of the chain construction of high polymer molecules. We may impose, for instance, the most strict conditions that the distances of successive carbon atoms are all constant and that the successive carbon bonds can only rotate about the preceding bond with a clearly defined bond angle and a suitable hindering potential energy. The potential energy $V_0(S_{j,\lambda})$ also contains the interaction between different molecules, however, we shall not go into any detailed discussion of the form of the potential energy function and we are satisfied only with a formal treatment of the problem for the present purpose.

The potential energy due to the applied field is

$$V_F = -e^* \sum_{(j=1, \dots, N, \lambda=1, 2)} a_{j,\lambda} S_{2j,\lambda} \cdot \mathbf{F} \quad (2.5)$$

where

$$\left. \begin{aligned} a_{j,1} &= 1, \quad a_{j,2} = -(M_0/M)^{1/2}, \\ j &= 1, 2, \dots, N, \end{aligned} \right\} \quad (2.6)$$

and $\mathbf{F}$ is the local field (in Onsager's sense) due to the external macroscopic field.

In the absence of the external field, there are many local equilibrium configurations, $(S_{j,\lambda}^0)$, of high polymer molecules which are

given as the solutions of a set of equations

$$\partial V_0 / \partial S_{j,\lambda} = 0, \quad j=1, \dots, 2N; \lambda=1, 2, 3, \quad (2.7)$$

with subsidiary conditions

$$\partial^2 V_0 / \partial S_{j,\lambda} \partial S_{k,\mu} > 0, \quad j, k=1, \dots, 2N; \lambda, \mu=1, 2, 3. \quad (2.8)$$

These equilibrium configurations are separated from each other by the potential barriers.

When the temperature is sufficiently low and the thermal fluctuation is not large enough for the high polymer molecule to make transitions from one equilibrium configuration to another, the molecule can only vibrate about a local equilibrium configuration. Under such circumstances there is almost no contribution to the electric polarization due to the reorientation of dipoles by the influence of the applied field. There is, however, a small contribution to the electric polarization due to

the displacement of the equilibrium positions of the dipoles by the applied field. The low temperature dielectric absorption (β -absorption) would be attributed to this vibrational motion of dipoles about local equilibrium configurations. At higher temperatures the thermal fluctuation becomes large and the transitions of dipoles from one equilibrium configuration to another become very frequent. This is the situation under which the orientational contribution to the electric polarization becomes possible by the influence of the external field. The high temperature dielectric absorption (α -absorption) would, therefore, be attributed to this orientational transition of dipoles by the applied field.

In order to describe the motion of high polymer molecules in the neighborhood of local equilibrium configuration we expand the potential energy function in the following way:

$$V_0(S_{j\lambda}) = V_0(S_{j\lambda}^0) + \frac{1}{2} \sum (S_{j\lambda} - S_{j\lambda}^0)(S_{k\mu} - S_{k\mu}^0): (\partial^2 V_0 / \partial S_{j\lambda} \partial S_{k\mu})_0 + V_1(S_{j\lambda} - S_{j\lambda}^0), \quad (2.9)$$

where $V_1(S_{j\lambda} - S_{j\lambda}^0)$ is the term which is of the higher order in $(S_{j\lambda} - S_{j\lambda}^0)$. Introducing a new coordinate system

$$\xi_{j\lambda} = S_{j\lambda} - S_{j\lambda}^0, \quad (2.10)$$

we can rewrite Eqs. (2.1), (2.4) and (2.5) as follows:

$$T = (M_0/2) \sum \dot{\xi}_{j\lambda}^2, \quad (2.11)$$

$$V = V_0(S_{j\lambda}^0) + \frac{1}{2} \sum \xi_{j\lambda} \xi_{k\mu}: V_{j\lambda k\mu} + V_F + V_1, \quad (2.12)$$

where

$$V_{j\lambda k\mu} = (\partial^2 V / \partial S_{j\lambda} \partial S_{k\mu})_0, \quad (2.13)$$

and

$$V_F = -e^* \sum a_{j\lambda} S_{2j,\lambda}^0 \cdot F - e^* \sum a_{j\lambda} \xi_{2j,\lambda} \cdot F. \quad (2.14)$$

We now introduce a suitably chosen orthogonal transformation

$$\xi_{j\lambda} = \sum_i \sum_\nu A_{j\lambda, i\nu}^* X_{i\nu} \quad (2.15)$$

which brings the quadratic part of the potential energy into a diagonal form

$$V_0 = V_0(S_{j\lambda}^0) + (M_0/2) \sum_i \sum_\nu \omega_{i\nu}^2 X_{i\nu}^2 + V_1(X_{i\nu}). \quad (2.16)$$

Using this coordinate system, we have

$$T = (M_0/2) \sum_\mu \sum_\nu \sum_i \dot{X}_{\mu\nu i}^2, \quad (2.17)$$

$$V_F = -e^* \sum_j \sum_\lambda a_{j\lambda} S_{2j\lambda}^0 r_i F - e^* \sum_i \sum_\nu b_{i\nu} X_{i\nu} r_i F, \quad (2.18)$$

where

$$b_{i\nu} = \sum_j \sum_\lambda a_{j\lambda} A_{2j,\lambda,i,\nu} \quad (2.19)$$

and γ_i 's ($i=1, 2, 3$) are the direction cosines of the direction of the applied field.

§ 3. The Frequency Spectrum of Molecular Vibrations in Dipolar High Polymers

In the preceding section the motion of high polymer molecules is decomposed into two distinct modes, one is a transition from one equilibrium configuration to another and the other is a vibration about an equilibrium configuration. In this section a further analysis of the vibrational motion about an equilibrium configuration will be proceeded.

The system under consideration consists of a large number of molecules of polyvinyl chloride each of which still has a large number of monomer units. The nature of interaction between atoms in different molecules is of short range van der Waals attraction at longer distances and of strong repulsion at shorter distances superposed with long range electrostatic interactions. The nature of interaction between atoms in a molecule is of the chemical bond, i.e. of extremely high stiffness. As is well known²⁾ the frequency spectrum of the molecular vibration of the normal n -paraffins in the most stable linear configuration which is found in the crystalline state consists of three distinct branches. The branch of the highest frequencies is for the stretching modes of the carbon skeleton, the branch of the second highest frequencies is for the bending modes of the tetrahedral angle of the carbon chain, and the branch of the lowest frequencies corresponds to the modes of out-of-plane vibrations.

All of these branches are in infrared region. Since the configuration of molecules in dipolar high polymers is quite different from the ordered linear arrangement of the carbon skeleton in normal n -paraffin crystal the vibrational frequency spectrum of dipolar high polymers would be also rather different from that of normal n -paraffin. The frequency spectrum would have a very low frequency branch because of the following two reasons. The first reason is due to the fact that in polyvinyl chloride heavy chlorine atoms are arranged periodically along the carbon skeleton. It is well known that, in a periodically

coupled dynamical system in which two unlike masses alternate the frequency spectrum will usually split into optical and acoustical branches. If we apply this analysis to the case of linear vinylic high polymers, we may surmise that three acoustical branches would come out of the original three branches of the frequency spectrum of normal n -paraffins. These three branches, however, would still be in infrared region, and the first reason might not be sufficient for insuring the possibility of obtaining a very low frequency spectrum. The second reason is more positive. In the above consideration the possibility of hindering rotation is neglected. In most high polymers the molecular arrangement is in a highly disordered state, and this state is one of the characteristics of high polymers. Furthermore there is a sufficient evidence that the thermal motion of a large group of atoms is highly excited at a so-called glass transition temperature. This means that the cooperative motion of large masses is possible at such high temperatures. This situation is well reflected in a large value of the activation energy of high temperature dielectric absorption. The motion of large masses should naturally be associated with the motion of very low frequencies even at the temperatures where the α -absorption mechanism is frozen. We may therefore, suppose that the frequency spectrum of molecular vibrations of high polymers consists mainly of two branches. The branch of high frequency is in infrared region and the branch of low frequency is in centimeter, in radio frequency or eventually in audio frequency region as the case may be. For the moment we can not draw any quantitative conclusion as to the existence of the very low frequency spectrum. We hope that this point would be discussed somewhat in detail in future.

§ 4. Distribution Function

We saw in § 2 that it is possible to specify the motion and configuration of high polymer molecules in terms of local equilibrium configuration $S_{j\lambda}^0$, and the velocity $\dot{X}_{\mu\nu}$ and the position $X_{\mu\nu}$ about the equilibrium configuration. This specification of molecular motion is, of course, of an approximate nature, since the expansion of the potential energy function about an equilibrium configuration is possible

only when the displacement is small. We shall presently show that this specification of the motion is sufficiently accurate. At low temperatures where the motion of high polymer molecules is excited only slightly, the transition from one local equilibrium configuration to another will not be so frequent as is the transition between various vibrational states. In this case it may be assumed that $S_{j\lambda}^0$ configuration is almost frozen. At high temperatures where the motion of high polymer molecule is highly excited, the transition between various local equilibrium configurations becomes very frequent, although the transition between vibrational states is also very frequent. In this case, the relaxation time τ for the establishment of equilibrium as to the vibrational degrees of freedom may be very much smaller than the period of configurational transition (transition between different $S_{j\lambda}^0$'s), and the equilibrium distribution for the vibrational degrees of freedom can be assumed, i.e. the detailed description of the vibrational motion with time is not necessary. Since there are very many solutions for the local equilibrium configurations, $S_{j\lambda}^0$'s, these $S_{j\lambda}^0$'s may distribute almost continuously in $S_{j\lambda}^0$ -space. Hence the transition between various configurations can be regarded as the diffusion motion in $6N \times 3$ dimensional $S_{j\lambda}^0$ -space. At intermediate temperatures the vibrational motion and the diffusion transition are correlated with each other, and the separation of motion of high polymer molecules into two distinct modes becomes difficult. Under this circumstance, however, the separation is still possible if we consider the response of high polymer molecules to the oscillating applied field.

For the applied field of very high frequencies, only the high frequency vibrational modes can respond to the field, and the transition between equilibrium configuration may be frozen because the transition is associated with the motion of large masses. This is only true when it is energetically more favorable to turn many dipoles at a time from one equilibrium configuration to another than to turn only a small number of dipoles at a time. This seems to be the case in polyvinyl chloride. It is observed that the apparent energy of activation for the high temperature dielectric absorption in normal long chain ke-

tones is about 1 Kcal/mole per one carbon chain⁵). The activation energy of high temperature dielectric absorption for polyvinyl chloride is about 80 Kcal/mole. This indicates that the transition from one equilibrium configuration to another is associated with the motion of about forty monomer units. When the frequency of the applied field is low, this configurational transition becomes possible because it has a sufficient thermal energy for the transition. In this case again it is not necessary to give a detailed specification of the vibrational motion, since the effect of vibrational motion is completely smoothed out in the time interval with which we are concerned in the low frequency range.

From the above considerations we may now assume that the total distribution function $F(S_{j\lambda}^0, X_{lv}, \dot{X}_{lv})$ can be factorized in the following way:

$$F(S_{j\lambda}^0, X_{lv}, \dot{X}_{lv}) = g(S_{j\lambda}^0) F_1(S_{j\lambda}^0; \dot{X}_{lv}, X_{lv}), \quad (4.1)$$

where $g(S_{j\lambda}^0)$ is the distribution function in configuration space $S_{j\lambda}^0$, and $F_1(S_{j\lambda}^0; X_{lv}, \dot{X}_{lv})$ is the distribution function for the system of harmonic oscillators. The function $F_1(S_{j\lambda}^0; X_{lv}, \dot{X}_{lv})$ may depend on the configuration $S_{j\lambda}^0$ only slightly, because all possible equilibrium configurations $S_{j\lambda}^0$'s would have almost the same energy. Thence we assume

$$F_1(S_{j\lambda}^0; X_{lv}, \dot{X}_{lv}) = F_1(X_{lv}, \dot{X}_{lv}). \quad (4.2)$$

The distribution function F_1 is further factorized into two parts:

$$F_1(X_{lv}, \dot{X}_{lv}) = f(X_{lv}, \dot{X}_{lv}) F_0(X_{m\mu}, \dot{X}_{m\mu}), \quad (4.3)$$

where $f(X_{lv}, \dot{X}_{lv})$ is the distribution function for the low frequency modes and $F_0(X_{m\mu}, \dot{X}_{m\mu})$ is for the high frequency modes of the molecular vibrations which was discussed in § 3. Since the high frequencies of molecular vibrations are in an infrared region, the relaxation time for the establishment of thermal equilibrium as to the high frequency vibrational degree of freedom is very much shorter than the time with which we are concerned in the radio frequency region, $F_0(X_{m\mu}, \dot{X}_{m\mu})$ is represented by an equilibrium distribution function.

A generalized Fokker-Planck equation for the system is now given by

$$\begin{aligned} & \frac{\partial g}{\partial t} f + g \frac{\partial f}{\partial t} + \sum \dot{S}_{j\lambda}^0 \frac{\partial g}{\partial S_{j\lambda}^0} f + g \sum \{ \ddot{X}_{i\nu} \cdot (\partial f / \partial \dot{X}_{i\nu}) + \dot{X}_{i\nu} \cdot (\partial f / \partial X_{i\nu}) \} \\ & = \left\{ K(S_{j\lambda}^0, X_{i\nu}, \dot{X}_{i\nu}; S_{j\lambda}^0, X'_{i\nu}, \dot{X}'_{i\nu}) g(S_{j\lambda}^0) f(X'_{i\nu}, \dot{X}'_{i\nu}) \right. \\ & \quad \left. - K(S_{j\lambda}^0, X'_{i\nu}, \dot{X}'_{i\nu}; S_{j\lambda}^0, X_{i\nu}, \dot{X}_{i\nu}) g(S_{j\lambda}^0) f(X_{i\nu}, \dot{X}_{i\nu}) d\{S_{j\lambda}^0\} d\{X'_{i\nu}\} d\{\dot{X}'_{i\nu}\} \right\}, \quad (4.4) \end{aligned}$$

where $K(S_{j\lambda}^0, X_{i\nu}, \dot{X}_{i\nu}; S_{j\lambda}^0, X'_{i\nu}, \dot{X}'_{i\nu})$ is the transition probability which throws the state $S_{j\lambda}^0, X'_{i\nu}, \dot{X}'_{i\nu}$ in $d\{S_{j\lambda}^0\}, d\{X'_{i\nu}\}, d\{\dot{X}'_{i\nu}\}$ into $S_{j\lambda}^0, X_{i\nu}, \dot{X}_{i\nu}$ by a collision. This transition is induced by collisions between high frequency oscillators and low frequency oscillators and also by a collisions between low frequency oscillators. In accordance with the factorization of the distribution function, K is also factorized as follows:

$$K = K_1(S_{j\lambda}^0; S_{j\lambda}^0) K_2(X_{i\nu}, \dot{X}_{i\nu}; X'_{i\nu}, \dot{X}'_{i\nu}). \quad (4.5)$$

The general forms for the transition probabilities which satisfy the conditions of micro-reversibility and detailed balance are

$$K_1(S_{j\lambda}^0; S_{j\lambda}^0) = L_1(S_{j\lambda}^0; S_{j\lambda}^0) \exp \{ \beta H(S_{j\lambda}^0) \}, \quad (4.6)$$

$$L_1(S_{j\lambda}^0; S_{j\lambda}^0) = L_1(S_{j\lambda}^0; S_{j\lambda}^0), \quad (4.7)$$

$$K_2(X_{i\nu}, \dot{X}_{i\nu}; X'_{i\nu}, \dot{X}'_{i\nu}) = L_2(X_{i\nu}, \dot{X}_{i\nu}; X'_{i\nu}, \dot{X}'_{i\nu}) \exp \{ \beta H(X'_{i\nu}, \dot{X}'_{i\nu}) \}, \quad (4.8)$$

$$L_2(X_{i\nu}, \dot{X}_{i\nu}; X'_{i\nu}, \dot{X}'_{i\nu}) = L_2(X'_{i\nu}, \dot{X}'_{i\nu}; X_{i\nu}, \dot{X}_{i\nu}). \quad (4.9)$$

At high temperatures, the motion of molecules is sufficiently excited, and at lower frequencies of an applied field, we may assume a thermal equilibrium distribution for the vibrational modes

$$f(X_{i\nu}, \dot{X}_{i\nu}) = A \exp -\beta H(X_{i\nu}, \dot{X}_{i\nu}), \quad (4.10)$$

then the Eq. (4.4) becomes

$$\partial g / \partial t = \int [L_1(S_{j\lambda}^0; S_{j\lambda}^0) \exp \beta H(S_{j\lambda}^0) g(S_{j\lambda}^0) - L_1(S_{j\lambda}^0; S_{j\lambda}^0) \exp \beta H(S_{j\lambda}^0) g(S_{j\lambda}^0)] d\{S_{j\lambda}^0\}, \quad (4.11)$$

where we neglected the term which is proportional to $\dot{S}_{j\lambda}^0$. From this equation we obtain the high temperature dielectric behavior of high polymers. We need not discuss this behavior for the purpose of the present paper.

At lower temperatures, the motion of molecules is not sufficiently excited and the $S_{j\lambda}^0$ -transitions are frozen. We may hence introduce an approximation

$$L_1(S_{j\lambda}^0; S_{j\lambda}^0) = \delta(S_{j\lambda}^0 - S_{j\lambda}^0), \quad \partial g / \partial t = 0.$$

In this case the Eq. (4.4) becomes

$$\begin{aligned} & \partial f / \partial t + \sum \{ \ddot{X}_{i\nu} \cdot (\partial f / \partial \dot{X}_{i\nu}) + \dot{X}_{i\nu} \cdot (\partial f / \partial X_{i\nu}) \} \\ & = \int [L_2(X_{i\nu}, \dot{X}_{i\nu}; X'_{i\nu}, \dot{X}'_{i\nu}) \exp \{ \beta H(X'_{i\nu}, \dot{X}'_{i\nu}) \} f(X'_{i\nu}, \dot{X}'_{i\nu})] d\{X'_{i\nu}\} d\{\dot{X}'_{i\nu}\}. \quad (4.13) \end{aligned}$$

The right-hand side of this equation represents the effects of collisions on the distribution function. There are a several attempts to give a definite form for the collision term³⁾. Here we shall adopt the assumption which was introduced by Van Vleck and Weisskopf⁴⁾ and by Fröhlich⁵⁾ independently. That is

$$\partial f / \partial t + \sum \{ \ddot{X}_{i\nu} \cdot (\partial f / \partial \dot{X}_{i\nu}) + \dot{X}_{i\nu} \cdot (\partial f / \partial X_{i\nu}) \} = -(f - f_{eq}) / \tau, \quad (4.14)$$

The physical content of assumption (4.14) is that collisions tend to make the distribution to relax in a time τ to the equilibrium value, f_{eq} , characteristic of the instantaneous field at time t . f_{eq} is given by the following form

$$f_{eq} = C \exp \left[- \sum (M_0 \dot{X}_{i\gamma i}^2 + M_0 \omega_{i\gamma i}^2 X_{i\gamma i}^2 - 2e^* F X_{i\gamma i} \gamma_i) / 2kT \right]. \quad (4.15)$$

We may also adopt another form for the collision term which is suggested by Gross³⁾. The discussion on the different choices of the collision term will be given at the end of the next section.

§ 5. The Relation Between Low Frequency Vibrational Spectrum and the Low Temperature Dielectric Behavior

In § 4, we obtained an equation for the distribution function which describes the dynamical behavior of the system of harmonic oscillators. The solution is well known, and the complex dielectric constant is given by the following expression⁵⁾.

$$\epsilon(\omega) - \epsilon_\infty = \frac{4\pi e^{*2}}{3M_0} \sum_{i\gamma i} \frac{b_i^2}{\omega_{i\gamma i}^2} \cdot \frac{\omega_{i\gamma i}^2 \tau^2 + 1 - i\omega\tau}{\omega_{i\gamma i}^2 \tau^2 + (1 - i\omega\tau)} \quad (5.1)$$

If the frequency distribution of molecular vibration is sufficiently dense, the summation in Eq. (5.1) is replaced by the integration

$$\epsilon(\omega) - \epsilon_\infty = \frac{4\pi e^{*2}}{3M_0} \int_0^\infty \frac{g(\omega_0)}{\omega_0^2} \cdot \frac{\omega_0^2 - i(\omega\omega_1 + i\omega_1^2)}{\omega_0^2 - (\omega + i\omega_1)^2} d\omega_0, \quad (5.2)$$

where

$$\omega_1 = 1/\tau \quad (5.3)$$

is the relaxation frequency (reciprocal of the relaxation time τ). The static dielectric constant is given by

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi e^{*2}}{3M_0} \int_0^\infty \frac{g(\omega_0)}{\omega_0^2} d\omega_0. \quad (5.4)$$

Introducing an effective distribution function by

$$G(\omega_0) = \frac{4\pi e^{*2}}{3M_0} \cdot \frac{g(\omega_0)}{\omega_0^2}, \quad (5.5)$$

Eqs. (5.3), (5.4) are written in the following forms:

$$\epsilon(\omega) - \epsilon_0 = \frac{\omega}{2} \int_0^\infty G(\omega_0) \left[\frac{1}{\omega_0 - (\omega + i\omega_1)} - \frac{1}{\omega_0 + (\omega + i\omega_1)} \right] d\omega_0, \quad (5.6)$$

$$\epsilon_0 - \epsilon_\infty = \int_0^\infty G(\omega_0) d\omega_0. \quad (5.7)$$

Since $g(\omega_0)$ is defined for only positive values of ω_0 , it is possible to extend the definition of $g(\omega_0)$ to negative values of ω_0 by the condition

$$G(-\omega_0) = G(\omega_0). \quad (5.8)$$

Then Eq. (5.6) becomes

$$\epsilon(\omega) - \epsilon_0 = \frac{\omega}{2} \int_{-\infty}^\infty \frac{G(\omega_0)}{\omega_0 - (\omega + i\omega_1)} d\omega_0. \quad (5.7)$$

If we assume that there is no singularity of $G(\omega_0)$ on the complex ω_0 -plane, the path of integration can be shifted as is shown in Fig. 1. Then Eq. (5.7) becomes

$$\left. \begin{aligned} \varepsilon(\omega) - \varepsilon_0 &= \frac{\omega}{2} \left[\pi i G(\omega + i\omega_1) + P \int_{-\infty}^{\infty} \frac{G(\omega_0 + \omega + i\omega_1) d\omega_0}{\omega_0} \right], \\ \text{or} \quad \varepsilon(\omega - i\omega_1) - \varepsilon_0 &= \frac{(\omega - i\omega_1)}{2} \left[\pi i G(\omega) + P \int_{-\infty}^{\infty} \frac{G(\omega_0)}{\omega_0 - \omega} d\omega_0 \right]. \end{aligned} \right\} \quad (5.8)$$

For illustration we assume

$$G(\omega_0) = \frac{2}{\pi} \cdot \frac{\omega_2}{\omega_0^2 + \omega_m^2} (\varepsilon_0 - \varepsilon_{\infty}). \quad (5.9)$$

This gives

$$P \int_{-\infty}^{\infty} \frac{1}{\omega_0^2 + \omega_m^2} \cdot \frac{1}{\omega_0 - \omega} d\omega_0 = -\frac{\pi}{\omega_m} \cdot \frac{\omega}{\omega^2 + \omega_m^2}. \quad (5.10)$$

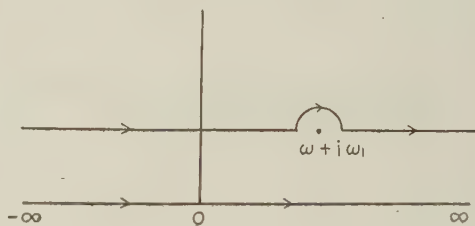


Fig. 1.

Introducing Eqs. (5.9), (5.10) into Eq. (5.8), and replacing ω by $\omega + i\omega_1$, we have

$$\frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon_0 - \varepsilon_{\infty}} = -\frac{\omega^2}{\omega_m} \cdot \frac{\omega}{\omega + i(\omega_m + \omega_1)}. \quad (5.11)$$

Separating real and imaginary parts, we obtain

$$\frac{\varepsilon_1(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{\omega_2}{\omega_m} \cdot \frac{(\omega_m + \omega_1)^2}{(\omega_m + \omega_1)^2 + \omega^2}, \quad (5.12)$$

$$\frac{\varepsilon_2(\omega)}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{\omega_2}{\omega_m} \cdot \frac{\omega(\omega_m + \omega_1)}{(\omega_m + \omega_1)^2 + \omega^2}. \quad (5.13)$$

These equations are of the Debye type, and the frequency of maximum absorption is given by $(\omega_m + \omega_1)$.

It is easy to generalize the above analysis to the case where the absorption curve is broader than that of Debye curve. We assume

$$\frac{G(\omega)}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{2}{\pi} \int_0^{\infty} \frac{y(\omega_0) d\omega_0}{\omega^2 + \omega_0^2}, \quad (5.14)$$

then

$$\left. \begin{aligned} \frac{1}{\varepsilon_0 - \varepsilon_{\infty}} P \int_{-\infty}^{\infty} \frac{G(\omega_1)}{\omega_1 - \omega} d\omega_1 &= \frac{2}{\pi} \int_0^{\infty} y(\omega_0) P \int_{-\infty}^{\infty} \frac{\omega_0}{\omega_1^2 + \omega_0^2} \cdot \frac{d\omega_1}{\omega_1 - \omega} = -2 \int_0^{\infty} \frac{y(\omega_0) \omega}{\omega^2 + \omega_0^2} d\omega_0, \\ \text{and} \quad \frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon_0 - \varepsilon_{\infty}} &= i\omega \int_0^{\infty} \frac{y(\omega_0) d\omega_0}{\omega_0 + \omega_1 - i\omega}. \end{aligned} \right\} \quad (5.15)$$

This result shows that the absorption curve and is represented by the superposition of Debye curves.

If we introduce the Stieltjes transform of $y(\omega_0)$ by

$$S(z) = \int_0^{\infty} \frac{y(x) dx}{x + z}, \quad (5.16)$$

then

$$\frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon_0 - \varepsilon_{\infty}} = i\omega S(-\omega_1 - i\omega), \quad (5.17)$$

$$G(\omega) = \frac{\varepsilon_0 - \varepsilon_{\infty}}{\pi} [S(-i\omega) + S(i\omega)]. \quad (5.18)$$

As is pointed out by Gross, the form of the collision term which is used in Eq. (4.15) is not appropriate from physical considerations. It assumes that the dipole will take up an equilibrium distribution within a relaxation time τ .

It is assumed that the collisions tend to

make the distribution to relax in a time τ to the equilibrium value which is characteristic of the instantaneous field at time t . This means that the dipole has to change its coordinate a finite amount within a collision. Gross introduced the assumption that the effect of collision is impulsive, i.e. the dipole does not change its coordinate but changes only its momentum within a collision. From this consideration he obtained the following expression for the dielectric constant

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{4\pi e^{*2}}{3M_0} \cdot \frac{1}{\omega_{iv1}^2 - \omega^2 - i\omega\omega_1} \quad (5.19)$$

In our case, the expression for the dielectric constant which corresponds to Eq. (5.2) becomes

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{4\pi e^{*2}}{3M_0} \int_0^\infty \frac{g(\omega_0) d\omega_0}{\omega_0^2 - \omega^2 - i\omega\omega_1} \quad (5.20)$$

We can obtain a relation between the distribution function and the dielectric constant in the same way as was done in Fröhlich's case.

From a mathematical point of view, it is equally possible to use Fröhlich's formula as well as Gross' formula in order to represent an observed dielectric constant by the superposition of many elementary absorption curves.

§ 6. Conclusion

The α -process is attributed, as has been done by many authors, to the orientational relaxation of dipoles, and the β -process is due to the vibrational relaxation of dipoles in the neighborhood of equilibrium configuration. Of course, the β -process is still excited at high temperatures where the α -process becomes possible, but the β -process is masked by the much larger α -process. In the case of polymonochlorotrifluoroethylene, however, the α -process is very small because of the small

resultant moment of monomer unit, and the β -process is dominant even at higher temperature where the α -process is sufficiently excited.

As is shown in § 5, it is possible to find a frequency distribution of molecular vibrations, but we can not show from the molecular theoretical consideration why the β -absorption should be found at such a low frequency region. We can interpret this only by a phenomenological consideration on the cooperation of very large number of monomer units. This point should be examined more carefully from a molecular theoretical consideration.

In the case of vinylic high polymers there is only one mode of orientational transition, i.e. the rotation of dipoles around the main carbon chain, and the α -process is attributed to this mode. But, in the case of polyalkylmethacrylate, there are two possibilities of the orientational transition of dipolar groups, i.e. the rotation around the main carbon chain and the rotation around the axis which is perpendicular to the main chain. These two modes may or may not cause two separate α -like absorptions. We have not sufficient experimental data to identify each absorption to each mode of rotation for the moment.

References

- 1) T. Tanaka and Y. Ishida: Prog. Theor. Phys. Sup. No. 10, (1959) 121.
- 2) J. G. Kirkwood: J. Chem. Phys. **7** (1939) 506.
- 3) E. P. Gross: Phys. Rev. **97** (1955) 395.
- 4) J. H. Van Vleck and V. Weisskopf: Rev. Mod. Phys. **17** (1945) 227.
- 5) H. Fröhlich: *Theory of Dielectrics* (Oxford Univ. Press, 1949).

Indirect Nuclear Spin-Spin Couplings in Saturated Hydrocarbon Molecules

By Eiko HIROIKE*

*Department of Physics, Tokyo Institute of Technology,
Oh-Okayama, Meguro, Tokyo*

(Received July 4, 1959)

A general formula for the coupling constant $J_{HH'}$ between two hydrogen nuclei is derived by means of the valence bond method. Almost all the structures, which are obtained by Rumer's theorem, are taken into account. The calculated value of $J_{HH'}$ in a methane molecule is 12.1 sec.⁻¹, which is in good agreement with experiment. It is shown that an approximate formula for $J_{HH'}$, which is derived from the general one, is convenient to discuss the qualitative behavior of $J_{HH'}$.

§ 1. Introduction

There are the molecular orbital (M.O.) and the valence bond (V.B.) methods in common use for the quantitative study of electronic states in molecules. As is well known, the former is convenient to discuss π -electron states in unsaturated hydrocarbon molecules. On the other hand, the latter is usually adopted to discuss σ -electron states in saturated hydrocarbon molecules, because the perfect pairing approximation in the V.B. method gives the simple and direct relation between chemical bonds and molecular stabilities. In the present paper we shall calculate the indirect nuclear spin-spin couplings in the saturated hydrocarbon molecules by means of the V.B. method.

In the V.B. method the ground state wave function Ψ is expressed as a linear combination of independent canonical structures Ψ_ξ 's obtained by Rumer's theorem. As is mentioned above, for the saturated hydrocarbon molecules there exists the perfect pairing structure Ψ_0 which is considered as a fairly good approximation to Ψ . Namely

$$\Psi = C_0 \Psi_0 + \sum_{\xi \neq 0} C_\xi \Psi_\xi, \quad (1)$$

where C_0 is nearly equal to unity and C_ξ 's ($\xi \neq 0$) are much smaller than unity, if Ψ , Ψ_0 and Ψ_ξ 's ($\xi \neq 0$) are normalized. In the following, the valence bonds appearing in Ψ_0 will be called "chemical bonds" and the other valence bonds, which do not appear in Ψ_0 but may appear in the other canonical structures, will be called "non-chemical bonds."

It is of interest to know the magnitude of C_ξ 's ($\xi \neq 0$), since it measures the degree of the bond delocalization. In principle C_ξ 's can be determined so as to minimize the ground state energy. It is, however, difficult to do so in large molecules, since our knowledge of the values of exchange integrals is not complete in such cases. Therefore it is desirable to find a method of determining C_ξ 's even if empirically. One method may be to use the indirect spin-spin coupling constant $J_{HH'}$ between two protons not directly bonded to one another by the "chemical bond," because, as will be seen in the following sections, $J_{HH'}$ is directly related to C_ξ 's.

Ramsey¹⁾ has shown that the interaction in a molecule between two proton spins, I_H and $I_{H'}$ (in units of $\hbar$), of the form

$$h J_{HH'} I_H \cdot I_{H'},$$

can be derived via the magnetic interaction between the protons and the electrons. He showed also that only the Fermi interaction makes an important contribution to $J_{HH'}$. By the use of second-order perturbation theory and also by the use of the approximation replacing energy differences between the ground state and the excited states by their suitable average, he derived the following formula:

$$J_{HH'} = -\frac{2}{3\hbar} (8\beta\hbar/3)^2 r_p^2 (\Delta E)^{-1} \times \langle \Psi | \sum_{i,j} \delta(r_{iH}) \delta(r_{jH'}) S_i \cdot S_j | \Psi \rangle. \quad (2)$$

β is the Bohr magneton, r_p the gyromagnetic ratio of proton, ΔE the suitable average of energy differences mentioned above, S_i the spin (in units of $\hbar$) of electron i , and r_{iH} is

* née Aihara.

$\mathbf{r}_i - \mathbf{r}_H$ where $\mathbf{r}_i$ and $\mathbf{r}_H$ denote the position vectors of electron i and proton H respectively.

Formula (2) is the fundamental expression on which all the calculations in the present paper are based. By using the M.O. method, McConnell²⁾ made a calculation of $J_{HH'}$ based on (2). However, the order of magnitude of the calculated $J_{HH'}$ for methane molecule did not coincide with that of observed one. The calculation by means of the V.B. method was made by us³⁾. We adopted Ψ which is a linear combination of two important structures and obtained the results in fairly good agreement with experiment. The purpose of the present paper is to improve our previous work by taking account of almost all canonical structures obtained via Rumer's theorem. Recently Karplus and Anderson⁴⁾ have made a similar calculation with the assumption of orthogonality of the atomic orbitals and of neglect of all the ionic structures. No such simplification will be made in our calculation.

In § 2 we shall give the general formula for $J_{HH'}$ by classifying the canonical structures into several groups. In § 3 we shall give an approximate formula for $J_{HH'}$ and discuss it. In § 4 some qualitative properties of $J_{HH'}$ will be discussed by the use of the approximate formula. In § 5 a numerical application of our formula to methane will be made.

§ 2. General Formula

Substituting (1) in (2), we find

$$J_{HH'} = -\frac{2}{3h} (8\beta h/3)^2 \gamma_p^2 (\Delta E)^{-1} \sum_{\xi, \eta} C_\xi C_\eta Q_{\xi, \eta}, \quad (3)$$

where

$$Q_{\xi, \eta} = (\Psi_\xi | Q | \Psi_\eta) \quad (4)$$

and

$$Q = \sum_{i,j} \delta(\mathbf{r}_{iH}) \delta(\mathbf{r}_{jH'}) \mathbf{S}_i \cdot \mathbf{S}_j. \quad (5)$$

In order to obtain explicit forms of $Q_{\xi, \eta}$'s, we shall first divide the canonical structures into several groups. Let the molecule under consideration have R chemical bonds. The atomic orbitals (A.O.'s) of the atoms H and H' are denoted by h and h' respectively. The A.O. pairing with h (h') to form a chemical bond is denoted by x (x'). The pairs of A.O.'s forming the other chemical bonds are denoted by b_ν and $b_{\nu'}$ ($\nu=3, 4, \dots, R$).

Ψ_ξ 's can be represented by means of Rumer diagrams⁵⁾ (R.D.'s) in which the arrangement

of the A.O.'s may be arbitrary. For the sake of convenience we align the A.O.'s on a circle in such a way that h and h' are neighbouring each other and the pairs of A.O.'s forming the chemical bonds also neighbouring each other, as illustrated in Fig. 1. The R.D. of each canonical structure is drawn on Fig. 1.

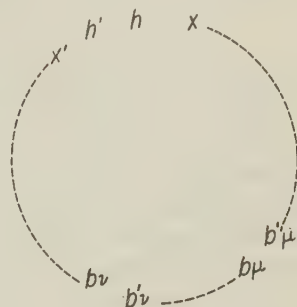


Fig. 1. Arrangement of the A.O.'s, on which the R.D. of each canonical structure is drawn. $hx, h'x', b_\mu b_{\mu'}, b_\nu b_{\nu'}$: the chemical bonds.

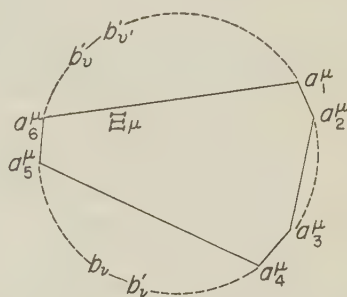


Fig. 2. Superposed diagrams of Ψ_0 and Ψ_ξ . $a_1^\mu - a_2^\mu$, $a_3^\mu - a_4^\mu$ and $a_5^\mu - a_6^\mu$ are chemical bonds in Ψ_0 . $a_2^\mu - a_3^\mu$, $a_4^\mu - a_5^\mu$ and $a_6^\mu - a_1^\mu$ are non-chemical bonds in Ψ_ξ . $b_\nu - b_{\nu'}$ and $b_{\nu'} - b_{\nu''}$ are common chemical bonds in Ψ_0 and Ψ_ξ .

We consider a structure Ψ_ξ which has $(R-M)$ chemical bonds and M non-chemical bonds. Superposing the R.D. of Ψ_ξ on the R.D. of Ψ_0 , we obtain several isolated lines and polygons. The formers are the common chemical bonds in Ψ_0 and Ψ_ξ . The latters are expressed hereafter by Ξ_μ ($\mu=1, 2, \dots, \lambda$), the sides of which are either the non-chemical bonds in Ψ_ξ or the chemical bonds in Ψ_0 (see Fig. 2).

Thus, all the structures appearing in (1) are divided into groups characterized by M (the number of the non-chemical bonds) and λ (the number of the polygons). In particular the group characterized by $M=0$, $\lambda=0$ contains only one structure, i.e. Ψ_0 . We divide the

structures in a group characterized by M and λ further into two groups: the group A contains the structures involving $h-h'$ bond and the group B the structures not involving $h-h'$ bond. We denote the structures in A and B by $\Psi_{M\lambda a}$ and $\Psi_{M\lambda b}$, and their coefficients in Ψ by $C_{M\lambda a}$ and $C_{M\lambda b}$, respectively.

Next task is to determine the explicit forms of $\Psi_{M\lambda a}$ and $\Psi_{M\lambda b}$. We shall call the orbital part of a wave function which represents the singlet state of two electrons localized in a (chemical or non-chemical) bond "bond function (B.F.)" and assume the following form for it.

$$\phi_{bd}(1, 2) = N(bd) \{b(1)d(2) + d(1)b(2) + I(b)b(1)b(2) + I(d)d(1)d(2)\}, \quad (6)$$

where $N(bd)$ is a normalization constant, b and d are the pair of A.O.'s forming this bond and $I(b)$ and $I(d)$ the coefficients of the ionic terms. When this bond is the non-chemical one, the ionic terms in the above expression will be neglected in the following calculation. This means the neglect of the ionic structures corresponding to the polarization of electrons from a chemical bond to another chemical bond. Such polarization may be considered to be less important as compared with the polarization in the same chemical bond.

We construct $\Psi_{M\lambda a(b)}$ from B.F.'s in the following manner:

$$\Psi_{M\lambda a(b)} = ((2R)!)^{-1/2} \sum_P (-)^P P(\Phi_{M\lambda a(b)} \cdot \Theta). \quad (7)$$

P is a permutation operator of electrons. Θ is a product of spin functions such as

$$\Theta = \alpha(1)\beta(2)\alpha(3)\beta(4) \cdots \alpha(2R-1)\beta(2R), \quad (8)$$

where α and β are the spin functions corresponding to one-electron spin components of $+1/2$ and $-1/2$ (in units of $\hbar$), respectively. $\Phi_{M\lambda a(b)}$ is the simple product of B.F.'s, namely

$$\begin{aligned} \Phi_{M\lambda a(b)} = & \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \left(1 - \frac{S^2(a_{2j-1}^{\mu} a_{2j}^{\mu})}{2} \right)^{-1/2} \prod_{\mu=1}^{\lambda} \{ \phi_{a_2^{\mu} a_3^{\mu}}(k_{\mu}+1, k_{\mu}+2) \\ & \times \phi_{a_4^{\mu} a_5^{\mu}}(k_{\mu}+3, k_{\mu}+4) \cdots \phi_{a_m^{\mu} a_1^{\mu}}(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}) \} \prod_{\nu=M+1}^R \phi_{b_{\nu} b_{\nu'}}(2\nu-1, 2\nu), \end{aligned} \quad (9)$$

where m_{μ} is the number of the sides of polygon Ξ_{μ} , $a_1^{\mu}, a_2^{\mu}, \dots, a_{m_{\mu}}^{\mu}$ are the A.O.'s on the corners of Ξ_{μ} numbered at in Fig. 2, $S(bb') = \int bb' d\tau$ and $k_{\mu} = \sum_{\nu=1}^{\mu-1} m_{\nu}$. $\Psi_{M\lambda a(b)}$, given by (7), are nearly normalized, because the overlap integrals between not chemically bonded A.O.'s, which will be denoted by T in the following, are much smaller than $S(a_{2j-1}^{\mu} a_{2j}^{\mu})$.

In general, when $\Psi_{\xi} = ((2R)!)^{-1/2} \sum_P (-)^P P(\Phi_{\xi} \cdot \Theta)$, we find the following expression by substituting Ψ_{ξ} in (4),

$$Q_{\xi, \eta} = \sum_P (-)^P \sum_{i,j} A_{\xi, \eta}(P; iH, jH') (\Theta | S_i \cdot S_j | P\Theta), \quad (10)$$

where

$$A_{\xi, \eta}(P; iH, jH') = (\Phi_{\xi} | \delta(r_{iH}) \delta(r_{jH'}) | P\Phi_{\eta}). \quad (11)$$

As is seen from (8), $(\Theta | P\Theta)$ is unity when $P=UV$ and zero otherwise, where U (V) is a permutation of odd (even) numbered electrons. Using the fact that

$$(\Theta | S_i \cdot S_i | P\Theta) = \frac{3}{4} (\Theta | P\Theta)$$

and

$$(\Theta | S_i \cdot S_j | P\Theta) = \frac{1}{2} (\Theta | (ij) P\Theta) - \frac{1}{4} (\Theta | P\Theta)$$

we obtain the non-zero values of $(\Theta | S_i \cdot S_i | P\Theta)$ and $(\Theta | S_i \cdot S_j | P\Theta)$ as follows;

$$(\Theta|S_i \cdot S_i|UV\Theta) = \frac{3}{4},$$

$$(\Theta|S_i \cdot S_j|UV\Theta) = (-)^{i+j} \frac{1}{4},$$

and

$$(\Theta|S_i \cdot S_j|(ij)UV\Theta) = \frac{1}{2} \quad \text{for } i+j = \text{odd number.}$$

Substituting the above results into (10), we obtain

$$\begin{aligned} Q_{\xi, \eta} = & \frac{3}{4} \sum_i \sum_{UV} (-)^{UV} \mathcal{A}_{\xi, \eta}(UV; iH, iH') - \frac{1}{2} \sum_{i+j=\text{odd}} \sum_{UV} (-)^{UV} \mathcal{A}_{\xi, \eta}((ij)UV; iH, jH') \\ & + \frac{1}{4} \sum_{i \neq j} \sum_{UV} (-)^{i+j} (-)^{UV} \mathcal{A}_{\xi, \eta}(UV; iH, jH'). \end{aligned} \quad (12)$$

We calculate $\mathcal{A}_{\xi, \eta}(P; iH, jH')$'s by the use of Φ_{ξ} 's given by (9) and substitute them in (12). In the calculation the contributions to the electron density at nucleus H (H') from A.O.'s other than h (h') are neglected, because they are very small. Therefore the first sum on the right-hand side of (12) are neglected for every case. Namely we adopt the following expression

$$Q_{\xi, \eta} = -\frac{1}{2} \sum_{i+j=\text{odd}} \sum_{UV} (-)^{UV} \mathcal{A}_{\xi, \eta}((ij)UV; iH, jH') + \frac{1}{4} \sum_{i \neq j} \sum_{UV} (-)^{i+j} (-)^{UV} \mathcal{A}_{\xi, \eta}(UV; iH, jH'). \quad (12')$$

According to our classification of the structures, (3) is written in a form:

$$\begin{aligned} J_{HH'} = & -\frac{2}{3h} (8\beta h/3)^2 \gamma^2 (4E)^{-1} \{ 2C_0 \sum_{M\lambda a} C_{M\lambda a} Q_{M\lambda a, 0} + C_0^2 Q_{00} \\ & + 2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b, 0} + \sum_{M\lambda a, M'\lambda' a'} C_{M\lambda a} C_{M'\lambda' a'} Q_{M\lambda a, M'\lambda' a'} \\ & + 2 \sum_{M\lambda a, M'\lambda' b'} C_{M\lambda a} C_{M'\lambda' b'} Q_{M\lambda a, M'\lambda' b'} + \sum_{M\lambda b, M'\lambda' b'} C_{M\lambda b} C_{M'\lambda' b'} Q_{M\lambda b, M'\lambda' b'} \}. \end{aligned} \quad (13)$$

Q_{00} , $Q_{M\lambda a, 0}$ and so on can be calculated by the use of (12'), (11), (9) and (6). Details of the calculation are given in Appendix A. The results are as follows:

$$Q_{00} = -\frac{3}{2} N^2(hx) N^2(h'x') \{ T(xx') + I(h)T(hx') + I(h')T(h'x) + I(h)I(h')T(hh') \} h^2(0)h'^2(0), \quad (14)$$

where $h^2(0)$ is the value of h^2 at the nucleus H and $T(xx') = \int xx' d\tau$, and so on.

$$\begin{aligned} Q_{M\lambda a, 0} = & 3 \times 2^{\lambda - (M/2) - 2} (-)^{M - \lambda + 1} N(hx) N(h'x') \\ & \times (1 + I(h)S(hx))(1 + I(h')S(h'x')) \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \left(1 - \frac{S^2(a_{2j-1}^{\mu} a_{2j}^{\mu})}{2} \right)^{-1/2} \\ & \times \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} N(a_{2j-1}^{\mu} a_{2j}^{\mu}) A_{2j-1, 2j}^{\mu} h^2(0) h'^2(0), \end{aligned} \quad (15)$$

(except for bonds $h-x$ and $h'-x'$)

where

$$\begin{aligned} A_{2j-1, 2j}^{\mu} = & 1 + \{ I(a_{2j-1}^{\mu}) + I(a_{2j}^{\mu}) \} S(a_{2j-1}^{\mu} a_{2j}^{\mu}) + S^2(a_{2j-1}^{\mu} a_{2j}^{\mu}). \\ Q_{M\lambda b, 0} = & 3 \times 2^{\lambda - M - 3} (-)^{M - \lambda + 1} \left(1 - \frac{S^2}{2} \right)^{-M/2} (1 + S^2)^{(M/2) - 4} T^2 h^2(0) h'^2(0) \\ & \times \{ 1 + S + (m_1 - 1)(1 + S^2) \} \{ 1 + S + (m_2 - 1)(1 + S^2) \}. \end{aligned} \quad (16)$$

In (16) m_1 (m_2) is the number of the sides of a polygon if $h-x$ ($h'-x'$) is a side of the

polygon and is unity if $h-x$ ($h'-x'$) is an isolated line.

$$Q_{M\lambda\alpha, M'\lambda'\alpha'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2} \right) \right\}^{\xi/2} \left(1 - \frac{S^2}{2} \right)^{-2} h^2(0) h'^2(0). \quad (17)$$

$$Q_{M\lambda\alpha, M'\lambda'b'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2} \right) \right\}^{(\xi/2)-t'-t} \left(1 - \frac{S^2}{2} \right)^{-2} h^2(0) h'^2(0). \quad (18)$$

When both of h and h' are on the corners of one polygon,

$$Q_{M\lambda b, M'\lambda'b'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2} \right) \right\}^{(\xi/2)-t-t'} \left(1 - \frac{S^2}{2} \right)^{-2} h^2(0) h'^2(0). \quad (19)$$

Otherwise, $Q_{M\lambda b, M'\lambda'b'}$'s turn out to be of the order of T^2 , which can be neglected as compared with (19).

In (17), (18) and (19), $R-L$ and ω are the numbers of the isolated lines and polygons, respectively, in the superposed diagrams of Ψ_ξ and Ψ_η ($\xi, \eta \neq 0$) (in general, $M, M' \neq L$ and $\lambda, \lambda' \neq \omega$), and ξ is the number of the chemical bonds constructing the polygons. In (18) and (19), t (t') is equal to unity if $h-x$ ($h'-x'$) is the side of the polygon. Otherwise, it is zero.

In the calculation of $Q_{M\lambda b, 0}$, $Q_{M\lambda\alpha, M'\lambda'\alpha'}$, $Q_{M\lambda\alpha, M'\lambda'b'}$ and $Q_{M\lambda b, M'\lambda'b'}$, we have replaced $S(a_{2j-1}^\mu a_{2j}^\mu)$'s by their mean value S and also neglected all the ionic terms, because their contributions to $J_{HH'}$ are usually smaller than those of $Q_{M\lambda\alpha, 0}$'s (see the next section).

§ 3. Approximate Formula for $J_{HH'}$

If we neglect all the second order terms of C_ξ ($\xi \neq 0$) and T in (13), we obtain the following approximate expression for $J_{HH'}$:

$$J_{HH'} = -\frac{2}{3h} (8\beta h/3)^2 r_p^2 (\Delta E)^{-1} 2C_0 \sum_{M\lambda\alpha} C_{M\lambda\alpha} Q_{M\lambda\alpha, 0}. \quad (20)$$

In this section we shall compare the magnitude of neglected terms with (20) and discuss whether such terms may be neglected or not. For our purpose, it is often convenient to use the following expression for $Q_{M\lambda\alpha, 0}$, in place of (15),

$$Q_{M\lambda\alpha, 0} = 3 \times 2^{\lambda-M-2} (-)^{M-\lambda+1} \left(1 - \frac{S^2}{2} \right)^{-M/2} (1+S^2)^{(M/2)-2} h^2(0) h'^2(0), \quad (21)$$

which is derived from (15) by the neglect of all the ionic terms and by replacing $S(a_{2j-1}^\mu a_{2j}^\mu)$'s by S . Such a simplification will be allowed, since, as will be explained in § 4, the neglect of ionic terms does not alter the order of magnitude of $Q_{M\lambda\alpha, 0}$'s.

1. $C_0^2 Q_{00}$

In hydrocarbon molecules, the atoms, to which x and x' belong respectively, have larger electronegativities than hydrogen atom (for example they are carbons⁶⁾). Therefore $I(h)$ and $I(h')$ are fairly smaller than unity. In (20) the largest contribution comes from the term with $M=2$, $\lambda=1$, namely $2C_0 C_{21\alpha} Q_{21\alpha, 0}$, since, in general, $C_{M\lambda\alpha}$'s become much smaller as M increases. It is to be noted that there is only one A -structure with $M=2$ and $\lambda=1$. We may compare $C_0^2 Q_{00}$ with $2C_0 C_{21\alpha} Q_{21\alpha, 0}$. From (14) and (15) we obtain

$$|Q_{00}/Q_{21\alpha, 0}| \sim 2N(hx)N(h'x')T^2 \left(1 - \frac{S^2(hx)}{2} \right)^{1/2} \left(1 - \frac{S^2(h'x')}{2} \right)^{1/2}, \quad (22)$$

where we have assumed that T 's appearing in (14) are of the same order of magnitude and that S 's in (15) are of the order of unity. Since it is known that $S^2 \sim 1/2$ and $T^2 \sim 100^{-1}$, the above expression becomes

$$|Q_{00}/Q_{21\alpha, 0}| \sim 1/200.$$

Therefore we obtain

$$|C_0^2 Q_{00}/2C_0 C_{21\alpha} Q_{21\alpha,0}| \sim 1/400 |C_0/C_{21\alpha}|. \quad (23)$$

If both of H and H' atoms are chemically bonded to one atom, $T(xx')$ is zero (see (14)). In such a case the value of $|C_0^2 Q_{00}/2C_0 C_{21\alpha} Q_{21\alpha,0}|$ will be much smaller than the one given by (23). (23) shows that $|C_0^2 Q_{00}|$ is smaller than 10% of $|2C_0 C_{21\alpha} Q_{21\alpha,0}|$, provided $|C_{21\alpha}| > 1/40$. On the other hand it shows that $|C_0^2 Q_{00}|$ cannot be neglected, if $|C_{21\alpha}|$ is very small. In such a case we may calculate Q_{00} by the use of (14), since the calculation is not so difficult.

$$2. \quad 2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b,0}$$

Comparing (16) with (21) and considering that $S \sim 1$, we obtain

$$Q_{M\lambda b,0}/Q_{M\lambda\alpha,0} \sim (1/2)m_1 m_2 T^2. \quad (24)$$

It is noted that $m_1 m_2$ depends not only upon M and λ but also upon b . We shall replace $m_1 m_2$'s by their mean over b , which will be denoted as $\langle m_1 m_2 \rangle_{M\lambda}$. Since we are concerned here only with the estimation of the order of magnitude, $|C_{M\lambda\alpha}|$'s and $|C_{M\lambda b}|$'s may be considered to be of the same order of magnitude. Therefore we may write, by the use of (24), as

$$|2C_0 \sum_b C_{M\lambda b} Q_{M\lambda b,0}/2C_0 \sum_a C_{M\lambda\alpha} Q_{M\lambda\alpha,0}| \sim \frac{1}{2} T^2 \langle m_1 m_2 \rangle_{M\lambda} \{ (\sum_b)_{M\lambda} / (\sum_a)_{M\lambda} \}, \quad (25)$$

where $(\sum_a)_{M\lambda}$ and $(\sum_b)_{M\lambda}$ are the numbers of structures characterized by M, λ, A and M, λ, B , respectively. We can prove that

$$(\sum_b)_{M\lambda} / (\sum_a)_{M\lambda} \leq \{ R(R-1)/(M-1)(M-2\lambda+2) \} - 1, \quad (26)$$

Table I. The values of $(\max. m_1 m_2)_{M\lambda} \{ [R(R-1)/(M-1)(M-2\lambda+2)] - 1 \}$.

$M \backslash R \lambda$	2	3	4	4	5	5	6	6	6
	1	1	1	2	1	2	1	2	3
4	10	3.0	0.0	4.0	—	—	—	—	—
5	18	6.9	2.8	9.2	0.0	4.2	—	—	—
6	28	12.0	6.0	16.0	2.5	9.0	0.0	4.5	8.0
7	40	18.0	10.0	24.0	5.5	15.0	2.4	9.9	12.8
8	54	24.9	14.8	33.2	9.0	22.2	5.4	16.2	18.4
9	70	33.0	20.0	44.0	13.0	30.0	8.4	23.4	24.8
10	88	42.0	26.0	56.0	17.5	39.0	12.0	31.5	32.0
20	378	187.2	122.8	249.6	90.0	184.2	70.2	162.0	148.0

where the equality holds for $\lambda=1$. The proof of this relation will be omitted here. It is difficult to obtain $\langle m_1 m_2 \rangle_{M\lambda}$ for the general cases of M, λ , although $\langle m_1 m_2 \rangle_{M\lambda}$ is to be nearly equal to unity for $M \ll R$. However, as is shown in Table I, $(\max. m_1 m_2)_{M\lambda} (\sum_b)_{M\lambda} / (\sum_a)_{M\lambda}$ is the largest for $M=2, \lambda=1$. $(\max. m_1 m_2)_{M\lambda}$ means a maximum of $m_1 m_2$ with M and λ fixed and b varied. Therefore $\langle m_1 m_2 \rangle_{M\lambda} (\sum_b)_{M\lambda} / (\sum_a)_{M\lambda}$ will be also the largest for $M=2, \lambda=1$. We take notice also of the fact that $|C_{21\alpha}|$ and $|C_{21b}|$ are much larger than other $|C_{M\lambda\alpha}|$'s and $|C_{M\lambda b}|$'s, respectively. After all we can safely obtain the following relation

$$|2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b,0}/2C_0 \sum_{M\lambda\alpha} C_{M\lambda\alpha} Q_{M\lambda\alpha,0}| \sim \frac{1}{2} T^2 \langle m_1 m_2 \rangle_{2,1} \frac{(\sum_b)_{2,1}}{(\sum_a)_{2,1}} \sim \frac{1}{2} 10^{-2} \{ R(R-1)/2-1 \}. \quad (27)$$

(27) shows that $|2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b,0}|$ is smaller than 10% of $|2C_0 \sum_{M\lambda\alpha} C_{M\lambda\alpha} Q_{M\lambda\alpha,0}|$ for $R < 7$ and

that it is of the same order as the latter for $R \sim 20$.

$$3. \sum_{\xi, \eta \neq 0} C_{\xi} C_{\eta} Q_{\xi, \eta}$$

Comparing (17), (18) and (19) with (21) and using $S^2 \sim 1/2$, we see that $Q_{M\lambda a, M'\lambda' a'}$, $Q_{M\lambda a, M'\lambda' b'}$ and $Q_{M\lambda b, M'\lambda' b'}$ are of the same order as $Q_{M\lambda a, 0}$. Therefore we obtain

$$| \sum_{M\lambda a, M'\lambda' a'} C_{M\lambda a} C_{M'\lambda' a'} Q_{M\lambda a, M'\lambda' a'} | \sim \{ \sum_{M\lambda a} |C_{M\lambda a}| \}^2 \langle |Q| \rangle, \quad (28.1)$$

$$| \sum_{M\lambda a, M'\lambda' b'} C_{M\lambda a} C_{M'\lambda' b'} Q_{M\lambda a, M'\lambda' b'} | \sim (\sum_{M\lambda a, M'\lambda' b'} |C_{M\lambda a} C_{M'\lambda' b'}|) \langle |Q| \rangle, \quad (28.2)$$

$$| \sum_{M\lambda b, M'\lambda' b'} C_{M\lambda b} C_{M'\lambda' b'} Q_{M\lambda b, M'\lambda' b'} | \sim (\sum_{M\lambda b, M'\lambda' b'}^* |C_{M\lambda b} C_{M'\lambda' b'}|) \langle |Q| \rangle, \quad (28.3)$$

where we have replaced $Q_{M\lambda a, 0}$'s by their mean $\langle |Q| \rangle$, since the magnitude of $Q_{M\lambda a, 0}$ does not appreciably alter with M, λ . In (28.3) $\sum_{M\lambda b, M'\lambda' b'}^*$ means the sum for the cases where both of h and h' are on the corners of one polygon (see below (19)). Therefore the number of terms on the right-hand side of (28.3) is nearly equal to the one of (28.2) in spite of the fact that, in general, there exist much more B -structures than A -structures. A ratio of the numbers of terms in (28.3) and (28.2) with the same M, λ and M', λ' is shown in Table II for several values of M, λ, M', λ' and R . In most cases the ratio is of the order of unity.

Table II. The values of $\frac{\text{the number of terms in (28.3) with } M, \lambda, M', \lambda' *}{\text{the number of terms in (28.2) with } M, \lambda, M', \lambda'}$

M	λ	M	λ	R	4	5	6	7	8
2	1	2	1		0.80	0.66	0.58	0.50	0.44
3	1	2	1		0.66	0.70	0.66	0.62	0.56
3	1	3	1		0.50	0.86	0.94	0.94	0.90
4	1	2	1		0.00	0.40	0.52	0.54	0.52
4	1	3	1		0.00	0.46	0.74	0.86	0.88
4	2	2	1		1.02	0.78	0.64	0.54	0.48
4	2	3	1		0.90	1.06	0.98	0.88	0.82

* In general, $(\sum_a C_{M\lambda a})(\sum_b C_{M'\lambda' b})$ is not equal to $(\sum_a C_{M'\lambda' a})(\sum_b C_{M\lambda b})$. The number of terms in (28.2) with M, λ, M', λ' means $(\sum_a C_{M\lambda a})(\sum_b C_{M'\lambda' b}) + (\sum_a C_{M'\lambda' a})(\sum_b C_{M\lambda b})$.

Therefore (28.2) and (28.3) will be of the same order of magnitude, since $|C_{M\lambda a}|$'s and $|C_{M\lambda b}|$'s with the same M and λ are of the same order. Then we collect (28.1), (28.2) and (28.3) together and arrange them in a form:

$$| \sum_{\xi, \eta \neq 0} C_{\xi} C_{\eta} Q_{\xi, \eta} | \sim (\sum_{M\lambda a} |C_{M\lambda a}|) (\sum_{\xi \neq 0}^{\gamma} |C_{\xi}|) \langle |Q| \rangle. \quad (29)$$

Therefore we obtain

$$| \sum_{\xi, \eta \neq 0} C_{\xi} C_{\eta} Q_{\xi, \eta} | / | 2C_0 \sum_{M\lambda a} C_{M\lambda a} Q_{M\lambda a, 0} | \sim \sum_{\xi \neq 0}^{\gamma} |C_{\xi}| / |C_0|. \quad (30)$$

This expression is not so self-evident, because the numerator on the left-hand side is the sum over both of A - and B -structures while the denominator is the sum only over A -structures.

(30) shows that $\sum_{\xi, \eta \neq 0} C_{\xi} C_{\eta} Q_{\xi, \eta}$ can be neglected when $\sum_{\xi \neq 0}^{\gamma} |C_{\xi}|$ is small, as it should be. However, the condition that $\sum_{\xi \neq 0}^{\gamma} |C_{\xi}|$ is very small is in conflict with the condition to neglect

$C_0^2 Q_{00}$ (see (23)). It may be said that, when $|C_{21a}| \sim 1/30$, both of $C_0^2 Q_{00}$ and $\sum_{\xi, \eta \neq 0} C_\xi C_\eta Q_{\xi, \eta}$ can be neglected. A methane molecule is the case, in which $\sum_{\xi \neq 0} |C_\xi| \sim 0.17$ and $|C_{21a}| \sim 0.027^*$.

In this section we have discussed with the assumption that all the $C_\xi C_\eta Q_{\xi, \eta}$'s have the same sign. In fact they may be either positive or negative. This fact will favor the validity of the approximate formula (20), because errors owing to the neglect of $2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b, 0}$ and $\sum_{\xi, \eta \neq 0} C_\xi C_\eta Q_{\xi, \eta}$ may be smaller than the above estimation.

§ 4. Qualitative Behavior of $J_{HH'}$

We know, from experiments^{7), 8)}, that $J_{HH'}$ decreases as a distance between H and H' increases and also that $J_{HH'}$ decreases as an electronegativity of the atom, which is chemically bonded to H or H', becomes large. As is shown in the following, these experimental facts can be explained with the help of (20).

1) *Dependence of $J_{HH'}$ on $R_{HH'}$* ($R_{HH'}$ is a distance between atoms H and H'). It is seen, from (15), that $Q_{M\lambda a, 0}$'s are independent of $R_{HH'}$. Therefore the dependence of $J_{HH'}$ is determined by the behavior of $C_{M\lambda a}$'s (see (20)). We have calculated them approximately by the use of the simple V.B. method. The calculation is made in Appendix B. Using (B.4) in Appendix B, we obtain in particular

$$C_{21a} \approx -\{(xx') + (hh') - (xh') - (hx')\} / 2\{(xh) + (x'h')\} \quad (31)$$

and

$$C_{31a} \approx \frac{\{(xx') + (hh') - (xh') - (hx') + (xb') + (h'b') + (hb') + (x'b) - (xb) - (h'b) - (hb') - (x'b')\}}{4\{(xh) + (x'h') + (bb')\}}. \quad (32)$$

In (32), b and b' are A.O.'s forming a chemical bond other than $h-x$ and $h'-x'$ (see Fig. 1). (xx') , for example, means the exchange integral between A.O.'s x and x' . Since the denominators of (31) and (32) are independent of $R_{HH'}$, we must investigate only the numerators.

Let us consider the case that $R_{HH'}$ increases. Then (xx') , (hh') , (hx') and $(h'x)$ decrease. The other exchange integrals, appearing in the numerator of (32), namely (xb') and (hb') etc., will also decrease, because in most cases the chemical bond $b-b'$ will be far from both of $h-x$ and $h'-x'$. Therefore we may say that C_{21a} and C_{31a} decrease. It is seen, from (B.4), that other $C_{M\lambda a}$'s will also behave in a similar way as C_{21a} and C_{31a} . It means that $J_{HH'}$ decreases as $R_{HH'}$ increases.

Though the above discussion has been based on approximate formula (20), most terms appearing in (13) also have the same dependence on $R_{HH'}$ as (20). Namely the second term in (13) decreases as $R_{HH'}$ increases, since it is proportional to

$$\{T(xx') + I(h)T(hx') + I(h')T(h'x) + I(h)I(h')T(hh')\}^2$$

(see (14)). The fourth and fifth terms show the same behavior. Therefore it may be said that $J_{HH'}$ in general decreases as $R_{HH'}$ increases.

2) *Influence of ionic terms on $J_{HH'}$* . We shall assume that all the coefficients of ionic terms in B.F.'s (see (6)) are fairly small compared with unity. Then all C_ξ 's are almost independent of the presence of ionic terms. Since our discussion is based on (20), we investigate $Q_{M\lambda a, 0}$'s. As is seen from (15), they are proportional to

$$\prod_{b-b'} N(bb') A_{bb'} N(hx) \{1 + I(h)S(hx)\} N(h'x') \{1 + I(h')S(h'x')\},$$

where $b-b'$ is a chemical bond constructing a side of a polygon Ξ_μ .

Using that $S^2 \sim 1/2$, we obtain

* These values have been found by the use of the ground state wave function obtained by Karplus and Anderson⁴⁾.

$$N(bb')A_{bb'} \approx \frac{3}{2}^{1/2} \times \frac{\{1+0.47(I(b)+I(b'))\}}{\{1+0.47(I(b)+I(b'))+(1/6)(I^2(b)+I^2(b')+I(b)I(b'))\}} \quad (33)$$

As $(1/6)\{I^2(b)+I^2(b')+I(b)I(b')\} \ll 1$, (33) shows that $N(bb')A_{bb'}$ is almost independent of $I(b)$ and $I(b')$. On the other hand we obtain, by the use of $S^2 \sim 1/2$,

$$N(hx)\{1+I(h)S(hx)\} \approx 3^{-1/2} \times \frac{1+0.71I(h)}{1+0.47(I(h)+I(x))+(1/6)(I^2(h)+I^2(x)+I(h)I(x))} \quad (34)$$

and a similar expression for $N(h'x')\{1+I(h')S(h'x')\}$. It is seen, from (34), that $N(hx)\{1+I(h)S(hx)\}$ decreases as $I(x)$ increases. The increase of $I(x)$ means the increase of the electronegativity of the atom to which x belongs.

Therefore we obtain the conclusion that $J_{HH'}$ decreases as the electronegativity of the atom chemically bonded to H or H' increases. We can show, in a similar way as in 1) in this section, that this conclusion will not alter even if we adopt the general formula for $J_{HH'}$ in place of (20).

§ 5. Numerical Application to Methane Molecule and Discussion

We have applied general formula (13) for $J_{HH'}$ to a methane molecule. Using the ground state wave function obtained by Karplus and Anderson⁴⁾, we obtain the values of C_{ξ} 's. The values of $Q_{\xi,\eta}$'s are calculated by the use of (14), (15), (16), (17), (18) and (19). We adopt 1s Slater function for a hydrogen atom to calculate $h^2(0)$ and $h'^2(0)$, and $\Delta E=10$ eV. This value of ΔE has been adopted by many authors^{2), 4), 9)}. We assume that $I(h)=I(h')=0$ and take several values between 0 and 1/2 for $I(x)$ and $I(x')$, since their accurate values have not yet been known. The results of our calculations are shown in Table III.

Table III. The calculated values for CH₄ molecule.

$I_x=I_{x'}$	0	1/5	1/4	1/3	1/2
$C_0^2 Q_{00}$	0.00	0.00	0.00	0.00	0.00
$2C_0 C_{21\alpha} Q_{21\alpha,0}$	-1.83	-1.54	-1.46	-1.35	$-1.19 \times 10^{-2} h^2(0) h'^2(0)$
$2C_0 \sum C_{M\lambda\alpha} Q_{M\lambda\alpha,0}$	-0.18	-0.15	-0.14	-0.13	-0.12
$2C_0 \sum C_{M\lambda b} Q_{M\lambda b,0}$	-0.10	-0.10	-0.10	-0.10	-0.10
$\sum C_{M\lambda\alpha} C_{M'\lambda'\alpha'} Q_{M\lambda\alpha, M'\lambda'\alpha'}$	-0.11	-0.11	-0.11	-0.11	-0.11
$2 \sum C_{M\lambda\alpha} C_{M'\lambda'b'} Q_{M\lambda\alpha, M'\lambda'b'}$	-0.21	-0.19	-0.19	-0.18	-0.17
$\sum C_{M'\lambda b} C_{M'\lambda'b'} Q_{M\lambda b, M'\lambda'b'}$	-0.08	-0.07	-0.06	-0.06	-0.05
$(\Psi Q \Psi)$	-2.51	-2.16	-2.06	-1.93	-1.74
$J_{HH'}(\text{sec}^{-1})$	14.0	12.1	11.5	10.8	9.7

The observed value of $J_{HH'}$ is $12.4 \pm 0.6 \text{ sec}^{-1}$.⁸⁾ As is seen from Table III, the calculated value for $I(x)=I(x')=1/5$ is in best agreement with the observed one.

In general $C_{21\alpha}$ will be much larger than other $C_{M\lambda\alpha}$'s. Therefore (20) may be further simplified in the following:

$$J_{HH'} \sim -\frac{2}{3h} (8\beta h/3)^2 \tau p^2 (\Delta E)^{-1} 2C_0 C_{21\alpha} Q_{21\alpha,0} \quad (35)$$

This is the expression used in our previous paper³⁾. As is seen from Table III, the value of $2C_0 C_{21\alpha} Q_{21\alpha,0}$ is not so different from the value of $(\Psi|Q|\Psi)$. Therefore it may be said that (35) is fairly good approximation to $J_{HH'}$ in a methane molecule.

Apart from the case of dealing with simple molecules such as methane, it is very difficult in general to determine C_{ξ} 's by minimizing the energy. In such cases, it will be useful to determine the order of $C_{21\alpha}$ by using the observed value of $J_{HH'}$ and (35).

Karplus and Anderson¹⁾ have also calculated $J_{HH'}$ for a methane molecule and obtained the

value in good agreement with the observed one. However, their formula does not contain the terms $C_0^2 Q_{00}$ and $2C_0 \sum_{M\lambda b} C_{M\lambda b} Q_{M\lambda b, 0}$ appearing in our general formula. Therefore their formula may fail to give the correct results for some cases, for example, large molecules (see the discussion in § 3).

The author wishes to express her appreciation to Professor K. Niira and Dr. K. Ohata for their valuable discussions. A part of this work was supported by the Scientific Research Expenditure of the Ministry of Education.

Appendix A

We shall here calculate $Q_{00\alpha}$, $Q_{M\lambda, 0}$'s and so on to the lowest order of T in each case. Namely Q_{00} and $Q_{M\lambda b, 0}$'s are calculated to the second order of T and $Q_{M\lambda\alpha, 0}$'s and others to the zeroth order of T .

(1) Derivation of Q_{00} ((14))

Φ_0 is written in terms of B.F.'s as (see (9)):

$$\Phi_0 = \phi_{hx}(1, 2) \phi_{h'x'}(3, 4) \cdots \phi_{b_y b_y'}(2\nu-1, 2\nu) \cdots \phi_{b_R b_R'}(2R-1, 2R). \quad (\text{A.1})$$

As has been assumed in the text (see above (12')), we neglect the contributions to the electron density at nucleus H (H') from A.O.'s other than h (h'). Therefore when we substitute (A.1) into the expression for Δ_{00} ((11)), only the $\Delta_{00}(P; iH, jH')$'s for $i=1$ or 2 and $j=3$ or 4 do not vanish owing to the presence of $\delta(r_{iH})$ and $\delta(r_{jH'})$. Furthermore we assume to be able to neglect the contributions more than the second order to T to Q_{00} . This means that it is not necessary to consider a permutation P which permutes the electrons appearing in three or more B.F.'s. Therefore it is sufficient to consider only $\Delta_{00}((14)(13)(24); 1H, 4H')$ and $\Delta_{00}((23)(13)(24); 2H, 3H')$ in the first sum on the right-hand side of (12').

If an UV permutes neither electron 1 nor electron 2, we can prove that

$$\Delta_{00}(UV; 1H, 3H') = \Delta_{00}(UV; 2H, 3H')$$

and

$$\Delta_{00}(UV; 1H, 4H') = \Delta_{00}(UV; 2H, 4H'), \quad (\text{A.2})$$

because Φ_0 is invariant under the electron exchange (12). Therefore in the second sum on the right-hand side of (12') $\Delta_{00}(UV; iH, jH')$'s with UV 's which permute neither electron 1 nor electron 2 are cancelled each other owing to the presence of $(-)^{i+j}$ and do not contribute to the sum. The same holds for $\Delta_{00}(UV; iH, jH')$'s with UV 's which permute neither electron 3 nor electron 4. Furthermore $\Delta_{00}(UV; iH, jH')$'s with UV 's which permute electron i or electron j vanish because of the presence of $\delta(r_{iH})$ and $\delta(r_{jH'})$. Therefore, neglecting the contributions more than the second order of T , we must consider only $\Delta_{00}((24); 1H, 3H')$ and $\Delta_{00}((13); 2H, 4H')$ in the second sum of (12').

After all we must calculate the above-mentioned four Δ_{00} 's. It turns out that all of them are equal to

$$N^2(hx)N^2(h'x')\{T(xx') + I(h)T(hx') + I(h')T(h'x) + I(h)I(h')T(hh')\}^2 h^2(0)h'^2(0). \quad (\text{A.3})$$

Substituting (A.3) into (12'), we obtain

$$Q_{00} = -\frac{3}{2} N^2(hx)N^2(h'x')\{T(xx') + I(h)T(hx') + I(h')T(h'x) + I(h)I(h')T(hh')\}^2 h^2(0)h'^2(0). \quad (\text{A.4})$$

(2) Derivation of $Q_{M\lambda\alpha, 0}$ ((15))

As has been explained in the text, there are λ polygons for $M\lambda A$ -structure, among which a polygon including $x-h-h'-x'$ as its sides is denoted by Ξ_1 in this paragraph. Following (9), we write $\Phi_{M\lambda\alpha}$ in a form:

$$\begin{aligned}
\mathcal{O}_{M\lambda\alpha} = & \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \{1 - S^2(a_{2j-1}^{\mu} a_{2j}^{\mu})/2\}^{-1/2} \times \phi_{hh'}(1, 2) \phi_{x'x}^1(3, 4) \cdots \phi_{m'x}^1(m_1-1, m_1) \\
& (a_1^1=x, a_1^2=h, a_3^1=h', a_4^1=x') \\
& \times \prod_{\mu=2}^{\lambda} \{ \phi_{a_2^{\mu} a_3^{\mu}}(k_{\mu}+1, k_{\mu}+2) \phi_{a_4^{\mu} a_5^{\mu}}(k_{\mu}+3, k_{\mu}+4) \cdots \phi_{a_{m-1}^{\mu} a_m^{\mu}}(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}) \\
& \times \prod_{\nu=M+1}^{\lambda} \phi_{b_{\nu} b_{\nu'}}(2\nu-1, 2\nu) \}. \tag{A.5}
\end{aligned}$$

For the sake of convenience we write $\mathcal{O}_0$ as follows:

$$\begin{aligned}
\mathcal{O}_0 = & \phi_{hx}(1, 2) \phi_{h'x'}(3, 4) \cdots \phi_{a_{m-1}^1 a_m^1}(m_1-1, m_1) \\
& \times \prod_{\mu=2}^{\lambda} \phi_{a_2^{\mu} a_3^{\mu}}(k_{\mu}+1, k_{\mu}+2) \phi_{a_4^{\mu} a_5^{\mu}}(k_{\mu}+3, k_{\mu}+4) \cdots \phi_{a_{m-1}^{\mu} a_m^{\mu}}(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}) \\
& \times \prod_{\nu=M+1}^R \phi_{b_{\nu} b_{\nu'}}(2\nu-1, 2\nu) \}. \tag{A.6}
\end{aligned}$$

Substituting (A.5) and (A.6) into (11), we see, in a similar way as in $\mathcal{A}_{00}$, that allowed numbers of i and j in $\mathcal{A}_{M\lambda\alpha,0}(P; iH, jH')$ are 1 and 2. Since $\mathcal{O}_0$ and $\mathcal{O}_{M\lambda\alpha}$ are invariant under the electron exchange (12), we find

$$\mathcal{A}_{M\lambda\alpha,0}((12)UV; 1H, 2H') = \mathcal{A}_{M\lambda\alpha,0}(UV; 2H, 1H')$$

and

$$\mathcal{A}_{M\lambda\alpha,0}((12)UV; 2H, 1H') = \mathcal{A}_{M\lambda\alpha,0}(UV; 1H, 2H'). \tag{A.7}$$

Therefore (12') becomes

$$Q_{M\lambda\alpha,0} = -\frac{3}{4} \sum_{UV} (-)^{UV} \{ \mathcal{A}_{M\lambda\alpha,0}(UV; 1H, 2H') + \mathcal{A}_{M\lambda\alpha,0}(UV; 2H, 1H') \}. \tag{A.8}$$

We assume to take account of only the zeroth order of T . Therefore we may consider only the permutations UV 's which permute the electrons belonging to one polygon among themselves. Furthermore in the one polygon (μ -th polygon) we may consider only two permutations, one of which permutes only odd numbered electrons in cyclic by one and the other permutes only even numbered electrons in cyclic by one, namely cycles $(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}-3, \cdots, k_{\mu}+3, k_{\mu}+1)$ and $(k_{\mu}+m_{\mu}, k_{\mu}+m_{\mu}-2, \cdots, k_{\mu}+4, k_{\mu}+2)$. Polygon E_1 is exceptional. In this case the permutation which must be considered is cycle $(m_1, m_1-2, \cdots, 4, 2)$ if $i=1$ and $j=2$ and $(m_1-1, m_1-3, \cdots, 3, 1)$ if $i=2$ and $j=1$. The above facts is stated together as follows: When we take account of only the contributions to the zeroth order of T in $Q_{M\lambda\alpha,0}$, it is sufficient to consider the following permutations

$$UV = \prod_{\mu=1}^{\lambda} (k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}-3, \cdots, k_{\mu}+3, k_{\mu}+1)^{\gamma_{\mu}} (k_{\mu}+m_{\mu}, k_{\mu}+m_{\mu}-2, \cdots, k_{\mu}+4, k_{\mu}+2)^{\delta_{\mu}}, \tag{A.9}$$

where for $\mu \geq 2$ γ_{μ} 's and δ_{μ} 's are 0 or 1 and $\gamma_{\mu} + \delta_{\mu} = 1$, and for $\mu=1$, $\gamma_1=0$, $\delta_1=1$ if $i=1$, $j=2$ and $\gamma_1=1$, $\delta_1=0$ if $i=2$, $j=1$.

Substituting (A.5), (A.6) and (A.9) into (11), we obtain

$$\begin{aligned}
\mathcal{A}_{M\lambda\alpha,0}(UV; 1H, 2H') = & \mathcal{A}_{M\lambda\alpha,0}(UV; 2H, 1H') = 2^{-M/2} \prod_{\lambda=1}^{\mu} \prod_{j=1}^{m_{\mu}/2} \{1 - S^2(a_{2j-1}^{\mu} a_{2j}^{\mu})/2\}^{-1/2} \\
& \times N(hx)N(h'x') \{1 + I(h)S(hx)\} \{1 + I(h')S(h'x')\} \\
& \times \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \{N(a_{2j-1}^{\mu} a_{2j}^{\mu}) A_{2j-1,2j}^{\mu}\} h^2(0) h'^2(0), \tag{A.10} \\
& \text{(except for bonds } h-x \text{ and } h'-x')
\end{aligned}$$

where

$$A_{2j-1,2j}^{\mu} = 1 + \{I(a_{2j-1}^{\mu}) + I(a_{2j}^{\mu})\}S(a_{2j-1}^{\mu}a_{2j}^{\mu}) + S^2(a_{2j-1}^{\mu}a_{2j}^{\mu}).$$

Finally we obtain from (A.8)

$$\begin{aligned} Q_{M\lambda\alpha,0} = & -\frac{3}{4} 2^{\lambda-(M/2)} (-)^{M-\lambda+1} \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \{1 - S^2(a_{2j-1}^{\mu}a_{2j}^{\mu})/2\}^{-1/2} \\ & \times N(hx)N(h'x')\{1 + I(h)S(hx)\}\{1 + I(h')S(h'x')\} \\ & \times \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \{N(a_{2j-1}^{\mu}a_{2j}^{\mu})A_{2j-1,2j}^{\mu}\}h^2(0)h'^2(0). \quad (A.11) \end{aligned}$$

(except for bonds $h-x$ and $h'-x'$)

(3) Derivation of $Q_{M\lambda b,0}((16))$

In $M\lambda B$ -structure, $h-x$ and $h'-x'$ cannot be the sides of the same polygon. The polygon having the side $h-x$ is denoted by Ξ_1 and the one having $h'-x'$ by Ξ_2 . If $h-x$ or $h'-x'$ is an isolated line, we consider it as a polygon having two corners. By the use of (9), $\Phi_{M\lambda b}$ is written as

$$\begin{aligned} \Phi_{M\lambda b} = & \prod_{\mu=1}^{\lambda} \prod_{j=1}^{m_{\mu}/2} \{1 - S^2(a_{2j-1}^{\mu}a_{2j}^{\mu})/2\}^{-1/2} \times \phi_{h\alpha_3^1}(1, 2)\phi_{\alpha_4^1\alpha_5^1}(3, 4) \cdots \phi_{\alpha_m^1\alpha}(m_1-1, m_1) \\ & (a_1^1=x, a_2^1=h, a_1^2=x', a_2^2=h') \\ & \times \phi_{h'\alpha_3^2}(m_1+1, m_1+2)\phi_{\alpha_4^2\alpha_5^2}(m_1+3, m_1+4) \cdots \phi_{\alpha_m^2\alpha}(m_1+m_2-1, m_1+m_2) \\ & \times \prod_{\mu=3}^{\lambda+f} \{\phi_{\alpha_2^{\mu}\alpha_3^{\mu}}(k_{\mu}+1, k_{\mu}+2)\phi_{\alpha_4^{\mu}\alpha_5^{\mu}}(k_{\mu}+3, k_{\mu}+4) \cdots \phi_{\alpha_m^{\mu}\alpha_1^{\mu}}(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu})\} \\ & \times \prod_{\nu=M+f+1}^R \phi_{b_{\nu}b_{\nu}'}(2\nu-1, 2\nu), \quad (A.12) \end{aligned}$$

where $f=2$ if both of Ξ_1 and Ξ_2 are isolated lines, $f=1$ if one of them is an isolated line and $f=0$ otherwise. In the present purpose we write Φ_0 in a form

$$\begin{aligned} \Phi_0 = & \phi_{hx}(1, 2)\phi_{\alpha_3^1\alpha_4^1}(3, 4) \cdots \phi_{\alpha_{m-1}^1\alpha_m^1}(m_1-1, m_1) \\ & \times \phi_{h'x'}(m_1+1, m_1+2)\phi_{\alpha_3^2\alpha_4^2}(m_1+3, m_1+4) \cdots \phi_{\alpha_{m-1}^2\alpha_m^2}(m_1+m_2-1, m_1+m_2) \\ & \times \prod_{\mu=3}^{\lambda+f} \{\phi_{\alpha_2^{\mu}\alpha_3^{\mu}}(k_{\mu}+1, k_{\mu}+2)\phi_{\alpha_4^{\mu}\alpha_5^{\mu}}(k_{\mu}+3, k_{\mu}+4) \cdots \phi_{\alpha_m^{\mu}\alpha_1^{\mu}}(k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu})\} \\ & \times \prod_{\nu=M+f+1}^R \phi_{b_{\nu}b_{\nu}'}(2\nu-1, 2\nu). \quad (A.13) \end{aligned}$$

Using (A.12) and (A.13) in (11), we see, like before, that allowed numbers of i and j in $\Delta_{M\lambda b,0}(P; iH, jH')$ are 1 or 2 and m_1+1 or m_1+2 respectively. Therefore $\Delta_{M\lambda b,0}((ij)UV; iH, jH')$'s appearing in the first sum on the right-hand side of (12') give the contributions at most of order T^2 . In the case of $Q_{M\lambda b,0}$ these contributions cannot be neglected, because the contributions of the second sum also begin with order T^2 as will be shown in the following.

In quite an analagous way as in the derivation of (A.9), UV 's giving $\Delta_{M\lambda b,0}(UV; iH, jH')$ of the zeroth order of T , which are denoted by U_0V_0 , are

$$U_0V_0 = \prod_{\mu=1}^{\lambda+f} (k_{\mu}+m_{\mu}-1, k_{\mu}+m_{\mu}-3, \cdots, k_{\mu}+3, k_{\mu}+1)^{\gamma_{\mu}} (k_{\mu}+m_{\mu}, k_{\mu}+m_{\mu}-2, \cdots, k_{\mu}+4, k_{\mu}+2)^{\delta_{\mu}}, \quad (A.14)$$

where for $\mu \geq 3$ γ_{μ} 's and δ_{μ} 's are 0 or 1 and $\gamma_{\mu} + \delta_{\mu} = 1$, and for $\mu=1$, $\gamma_1=0$, $\delta_1=1$ if $i=1$ and $\gamma_1=1$, $\delta_1=0$ if $i=2$, and for $\mu=2$, $\gamma_2=0$, $\delta_2=1$ if $j=m_1+1$ and $\gamma_2=1$, $\delta_2=0$ if $j=m_1+2$.

By the use of the fact that Φ_0 and $\Phi_{M\lambda b}$ are invariant under the permutations $\prod_{r=1}^{m_1/2} (2r-1, 2r)$

and $\prod_{r=(m/2)+1}^{(m_1+m_2)/2} (2r-1, 2r)$, we can prove the following equation

$$\begin{aligned} \Delta_{M\lambda b,0}(U_0 V_0; 1H, m_1+1H') &= \Delta_{M\lambda b,0}(U_0 V_0; 1H, m_1+2H') \\ &= \Delta_{M\lambda b,0}(U_0 V_0; 2H, m_1+1H') = \Delta_{M\lambda b,0}(U_0 V_0; 2H, m_1+2H'). \end{aligned} \quad (A.15)$$

Therefore $\Delta_{M\lambda b,0}(U_0 V_0; iH, jH')$'s are cancelled each other in the second sum of (12') owing to the presence of $(-)^{i+j}$. In other words the second sum does not contain the terms of the zeroth order of T .

As is shown above, the leading terms of $Q_{M\lambda b,0}$ are of the second order of T . Therefore we may neglect all the ionic terms and replace $S(a_{2j-1}^\mu a_{2j}^\mu)$'s by their suitable mean S . The calculation of $Q_{M\lambda b,0}$ to the second order of T is lengthy but straightforward. Only the results will be cited in the following. In the second sum on the right-hand side of (12') the contribution to the second order of T arises from $\Delta_{M\lambda b,0}((2x, 2y)U_0 V_0; 1H, m_1+1H')$ and $\Delta_{M\lambda b,0}((2x-1, 2y-1)U_0 V_0; 2H, m_1+2H')$, where $2x$ denotes one of electrons $2, 4, \dots, m_1$ and $2y$ denotes one of electrons $m_1+2, m_1+4, \dots, m_1+m_2$. In the first sum of (12') the contribution under consideration arises from

$$\Delta_{M\lambda b,0}((1, m_1+2)UV; 1H, m_1+2H')$$

and

$$\Delta_{M\lambda b,0}((2, m_1+1)UV; 2H, m_1+1H'),$$

where

$$(1, m_1+2)UV = \prod_{r=1}^x \prod_{\tau=y+1}^{(m_1+m_2)/2} (2r-1, 2\tau)(2x-1, 2y-1)U_0 V_0(12)(m_1+1, m_1+2) \prod_{r=1}^x \prod_{\tau=y+1}^{(m_1+m_2)/2} (2r-1, 2\tau)$$

and

$$(2, m_1+1)UV = \prod_{r=1}^x \prod_{\tau=y+1}^{(m_1+m_2)/2} (2r-1, 2\tau)(2x, 2y)U_0 V_0(12)(m_1+1, m_1+2) \prod_{r=1}^x \prod_{\tau=y+1}^{(m_1+m_2)/2} (2r-1, 2\tau).$$

A final result is

$$\begin{aligned} Q_{M\lambda b,0} &= \frac{3}{2} (-)^{M-\lambda+1} 2^{\lambda-M-2} \left(1 - \frac{S^2}{2}\right)^{-M/2} (1+S^2)^{(M/2)-4} T^2 h^2(0) h'^2(0) \\ &\times \left\{ (1+S) + \left(\frac{m_1}{2} - 1\right)(1+S^2) \right\} \left\{ (1+S) + \left(\frac{m_2}{2} - 1\right)(1+S^2) \right\}. \end{aligned} \quad (A.16)$$

(4) *Derivation of $Q_{M\lambda\alpha, M'\lambda'\alpha'}$, $Q_{M\lambda\alpha, M'\lambda'b'}$ and $Q_{M\lambda b, M'\lambda'b'}$* ((17), (18) and (19))

The contribution of the above quantities to $J_{HH'}$ will be much smaller than those of $Q_{M\lambda\alpha,0}$'s, because $C_{M\lambda\alpha}$'s and $C_{M\lambda b}$'s are much smaller than C_0 (see (13)). Therefore in the calculation of these quantities we may neglect all the ionic terms and replace $S(a_{2j-1}^\mu a_{2j}^\mu)$'s by S .

When we superpose the R.D. of Ψ_ξ ($\xi \rightleftharpoons 0$) on the one of Ψ_η ($\eta \rightleftharpoons 0$) we obtain in general several isolated lines and polygons. We denote the latters by Γ_μ ($\mu=1, 2, \dots, \omega$). It is easily seen that the role of Γ_μ in the calculation of $Q_{\xi, \eta}$ ($\xi, \eta \rightleftharpoons 0$) is the same as the role of Ξ_μ in the calculation of $Q_{\xi, 0}$ ($\xi \rightleftharpoons 0$). Therefore we can calculate $Q_{\xi, \eta}$ ($\xi, \eta \rightleftharpoons 0$) in the same way as $Q_{\xi, 0}$ ($\xi \rightleftharpoons 0$), except that Γ_μ are not necessarily constructed by the equal numbers of the chemical bonds and the non-chemical bonds. (It is noted that in Ξ_μ the number of the chemical bonds is equal to the one of the non-chemical bonds.) We denote the sum of the numbers of sides of Γ_μ ($\mu=1, 2, \dots, \omega$) by $2L$ and the sum of the numbers of chemical bonds constructing Γ_μ by ζ . It should be noted that the number of isolated lines can be expressed by $R-L$.

In the case of $Q_{M\lambda\alpha, M'\lambda'\alpha'}$ the non-chemical bond $h-h'$ is included in both of structures $M\lambda\alpha$ and $M'\lambda'\alpha'$. Therefore $h-h'$ is always an isolated line. As in the calculation of $Q_{M\lambda\alpha,0}$, we obtain

$$Q_{M\lambda\alpha, M'\lambda'\alpha'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2}\right) \right\}^{\zeta/2} \left(1 - \frac{S^2}{2}\right)^{-2} h^2(0) h'^2(0). \quad (A.17)$$

In the case of $Q_{M\lambda a, M'\lambda' b'}$, $h-h'$ is a side of a polygon. This case can also be treated in a similar way as $Q_{M\lambda a, 0}$. We obtain

$$Q_{M\lambda a, M'\lambda' b'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2} \right) \right\}^{(\xi/2)-t'-t} \left(1 - \frac{S^2}{2} \right)^{-2} h^2(0) h'^2(0), \quad (\text{A.18})$$

where t (t') is equal to unity if $h-x$ ($h'-x'$) is included in $\Psi_{M'\lambda' b'}$ and zero otherwise.

In the calculation of $Q_{M\lambda b, M'\lambda' b'}$ we must consider the following two cases separately. In one case A.O.'s h and h' are on the corners of the different polygons. In such a case it can be proved in the same way as in $Q_{M\lambda b, 0}$ that the leading term of $Q_{M\lambda b, M'\lambda' b'}$ is of the second order of T . Therefore this case can be neglected. In the other case where h and h' are on the corners of the same polygon, the calculation can be made in a similar way as the one of $Q_{M\lambda a, 0}$. We obtain the following result:

$$Q_{M\lambda b, M'\lambda' b'} = 3 \times 2^{\omega-L-2} (-)^{L-\omega+1} \left\{ (1+S^2) / \left(1 - \frac{S^2}{2} \right) \right\}^{(\xi/2)-t-t'} \left(1 - \frac{S^2}{2} \right)^{-2} h^2(0) h'^2(0), \quad (\text{A.19})$$

where t (t') is equal to unity if $h-x$ ($h'-x'$) is included in $\Psi_{M\lambda b}$ or $\Psi_{M'\lambda' b'}$ and zero otherwise.

As will be seen from the above derivation, if we wish to take account of the ionic terms of the chemical bonds, we must replace $2^{-\xi/2}(1+S^2)^{\xi/2}$ in (A.17) by $\prod_{b-b'} N(bb') A_{bb'}$ and $2^{-\xi/2}(1+S^2)^{(\xi/2)-t-t'}$ in (A.18) and (A.19) by

$$\prod_{b-b'} N(bb') A_{bb'} \{N(hx)(1+I(h)S(hx))\}^t \{N(h'x')(1+I(h')S(h'x'))\}^{t'},$$

where $b-b'$'s are the chemical bonds, except for $h-x$ and $h'-x'$ constructing the polygons.

Appendix B

The ground state wave function of a molecule must have the form

$$\Psi = C_0 \Psi_0 + C_\xi^G \Psi_\xi^G + C_\eta^G \Psi_\eta^G + \dots \quad (\text{B.1})$$

Ψ_ξ^G is the wave function, which is invariant under the operations belonging to the point group of the molecular symmetry and is in connection with a canonical structure Ψ_ξ in the following manner:

$$\Psi_\xi^G = \sum_G G \Psi_\xi, \quad (\text{B.2})$$

where G 's are elements of the group. The group theory tells us that the identical terms appear g times in the sum of (B.2), where g is the number of elements satisfying $G \Psi_\xi = \Psi_\xi$. Therefore C_ξ appearing in (1) is connected with C_ξ^G by the relation $g C_\xi^G = C_\xi$.

Solving approximately the secular equation to determine the energy, we obtain

$$C_\xi^G \approx - \frac{(\Psi_\xi | \mathcal{H} | \Psi_0) - (\Psi_\xi | \Psi_0) (\Psi_0 | \mathcal{H} | \Psi_0)}{\sum_G \{ (G \Psi_\xi | \mathcal{H} | \Psi_\xi) - (G \Psi_\xi | \Psi_\xi) (\Psi_0 | \mathcal{H} | \Psi_0) \}} \quad (\text{B.3})$$

where $\mathcal{H}$ is the total Hamiltonian of the molecule. Matrix elements $(G \Psi_\xi | \mathcal{H} | \Psi_\xi)$ etc. are calculated by the simple V.B. method¹⁰⁾. Substituting them in (B.3), we obtain, for the canonical structure characterized by M, λ, A ,

$$C_{M\lambda a} \approx \frac{(-)^{M-\lambda} \sum_{\mu} \sum_{j \neq k} \{ (a_{2j-1}^\mu a_{2j}^\mu) - \frac{1}{2} (a_{2j-1}^\mu a_{2k-1}^\mu) - \frac{1}{2} (a_{2j}^\mu a_{2k}^\mu) \}}{2^{M-\lambda} \{ \sum_{\mu} \sum_j (a_{2j-1}^\mu a_{2j}^\mu) + \varepsilon \}} \quad (\text{B.4})$$

$(a_j a_k)$ is the exchange integral between A.O.'s a_j and a_k . ε is of the order of exchange integrals between A.O.'s not chemically bonded each other, which may be neglected compared with $(a_{2j-1}^\mu a_{2j}^\mu)$'s. The expression of $C_{M\lambda a}$ used in §3 is the one with the neglect of ε in (B.4).

References

- 1) N. F. Ramsey: Phys. Rev. **91** (1953) 303.
- 2) H. M. McConnell: J. Chem. Phys. **24** (1956) 460.
- 3) E. Aihara: J. Chem. Phys. **26** (1957) 1347.
- 4) M. Karplus and D. H. Anderson: J. Chem. Phys. **30** (1959) 6.
- 5) G. Rumer: Nachr. Ges. Wiss. Göttingen (1932) 337.
- 6) C. A. Coulson: *Valence* (Oxford Univ. Press, 1952) 134.
- 7) J. T. Arnold: Phys. Rev. **102** (1956) 136.
W. A. Anderson: *ibid.* **102** (1956) 151.
- 8) M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky: J. Chem. Phys. **27** (1957) 597.
- 9) G. A. Williams and H. S. Gutowsky: J. Chem. Phys. **30** (1959) 717.
- 10) H. Eyring, J. Walter and G. E. Kimball: *Quantum Chemistry* (John Wiley and Sons, 1944).

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

Potential Barrier of Phenol from its Microwave Spectrum

By Takeshi KOJIMA

Faculty of Literature and Science, Toyama University

(Received November 2, 1959)

The microwave spectrum of phenol, $C_6^{12}H_5O^{16}H$, was measured in the frequency range from 15 to 30 Gc/sec. A majority of the spectral lines was found to be doublet, which was explained as the effect of internal rotation of the OH-group in a hindering potential of the form $V=(V_2/2) \times (1-\cos 2x)$. The barrier height, V_2 , was determined to be 1100 ± 100 cm⁻¹ from the observed splittings.

By the use of a rigid rotor model, the effective rotational constants were calculated to be $A=5650.46$ Mc/sec, $B=2619.20$ Mc/sec and $C=1789.84$ Mc/sec. From these values, the OH-bond in its equilibrium configuration was found to lie on the plane comprising the C_6H_5 -group.

§ 1. Introduction

Recently the potential barrier hindering internal rotation has been precisely determined for a number of molecules¹⁾ by the use of microwave spectroscopy. In most of the molecules previously studied, the two parts of a molecule rotating relative to each other were found to be staggered in its equilibrium configuration. This was considered to be due to the dipole-quadrupole and quadrupole-quadrupole interactions²⁾ between the covalent bonds of one part and those of the other.

The OH-group of phenol may internally rotate relative to the C_6H_5 -group (Fig. 1). If its potential barrier is similar to that of methyl alcohol, the OH-bond in the equilibrium configuration will be out of the plane comprising the C_6H_5 -group. On the other hand, if the double bond character of the CO-bond

contributes dominantly to the formation of the barrier, the OH-bond will lie on the plane comprising the C_6H_5 -group. The latter consideration seems to be more plausible, but it has never been experimentally verified.

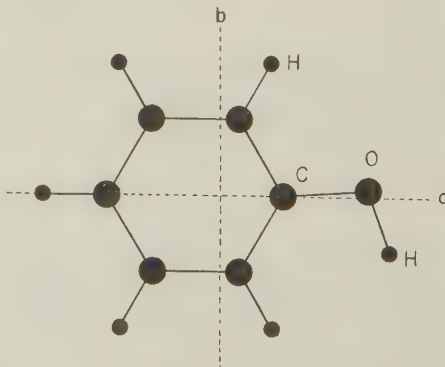


Fig. 1. Phenol molecule.

§ 2. Experiments and Results

The spectrum of phenol was measured in the frequency range from 15 to 30 Gc/sec. The spectrometer used was of the ordinary Stark-modulation type with X-band cell of five meters length. The measurement was carried out at room temperature, as the vapor pressure of phenol was high enough for our purpose.

More than two hundred lines were observed in the range. Most of the strong lines were found to be split into doublets due to the internal rotation of the OH-group relative to the C_6H_5 -group. The splitting of each doublet was about 112 Mc/sec.

The energy levels were calculated by the

Table I. Q-branch series of $C_6^{12}H_5O^{16}H$.

Transitions	Obs. freq. Mc/sec	Splitting Mc/sec	Center freq. Mc/sec	Calc. freq. Mc/sec
$4_{40} \leftarrow 4_{31}$	—*			23785.5
$5_{41} \leftarrow 5_{32}$	23383.7 23494.8	111.1	23439.3	23438.7
$6_{42} \leftarrow 6_{33}$	22689.5 22800.6	111.1	22745.0	22744.4
$7_{43} \leftarrow 7_{34}$	21546.5 21658.1	111.6	21602.3	21602.7
$8_{44} \leftarrow 8_{35}$	20032.5 20145.3	112.8	20088.9	20089.6
$9_{45} \leftarrow 9_{36}$	18460.5 18572.1	111.6	18516.3	18516.6
$10_{46} \leftarrow 10_{37}$	17284.4 17396.2	111.8	17340.3	17340.6
$11_{47} \leftarrow 11_{38}$	16945.3 17056.8	111.5	17002.0	17001.2
$12_{48} \leftarrow 12_{39}$	17752.3 17864.0	111.7	17808.2	17808.5
$4_{41} \leftarrow 4_{32}$	—*			23899.7
$5_{42} \leftarrow 5_{33}$	23814.0 23925.5	111.5	23869.7	23870.3
$6_{43} \leftarrow 6_{34}$	23867.2 23978.6	111.4	23922.9	23923.1
$7_{44} \leftarrow 7_{35}$	24095.4 24206.8	111.4	24151.1	24151.5
$8_{45} \leftarrow 8_{36}$	24604.4 24715.9	111.5	24660.1	24660.3
$9_{46} \leftarrow 9_{37}$	25489.4 25601.4	112.0	25545.4	25545.7
$10_{47} \leftarrow 10_{38}$	26821.7 26932.8	111.1	26877.3	26877.3
$11_{48} \leftarrow 11_{39}$	28629.7 28741.2	111.5	28685.5	28685.8

* These lines could not be observed because of their weak intensity.

use of a rigid rotor model, that is, on the assumption that the OH-group is rigidly fixed to the C_6H_5 -group and that the center frequency of doublet corresponds to the transition of the rigid rotor.

Two Q-branch series and several R-branch lines of *b*-type transition were identified. The assignments and the observed frequencies are listed in the first two columns of Tables I and II. From the center frequencies of these doublets the rotational constants (listed in Table III) were determined by the conventional method. The calculated frequencies were in good agreement with the observed values as shown in the last column in Tables I and II.

Table II. R-branch lines of $C_6^{12}H_5O^{16}H$.

Transitions	Obs. freq. Mc/sec	Splitting Mc/sec	Center freq. Mc/sec	Calc. freq. Mc/sec
$4_{04} \leftarrow 3_{13}$	14733.1 14844.9	111.8	14789.0	14789.11
$4_{14} \leftarrow 3_{03}$	17253.3 17365.1	111.8	17309.2	17309.11
$5_{05} \leftarrow 4_{14}$	18919.46 19031.50	112.04	18975.48	18975.52
$5_{15} \leftarrow 4_{04}$	20353.2 20465.3	112.1	20409.2	20409.25
$6_{03} \leftarrow 5_{15}$	22854.87 22967.07	112.20	22910.97	22911.05
$6_{16} \leftarrow 5_{05}$	23598.90 23710.65	112.25	23654.77	23654.73
$7_{07} \leftarrow 6_{16}$	26623.56 26735.31	111.75	26679.44	26679.52
$7_{17} \leftarrow 6_{06}$	26985.21 27097.02	111.81	27041.12	27040.79

Table III. Rotational constants of $C_6^{12}H_5O^{16}H$.

$A = 5650.46 \pm 0.20$ Mc/sec	$I_{a, \text{eff}} = 89.457$ amuA ²
$B = 2619.20 \pm 0.20$ Mc/sec	$I_{b, \text{eff}} = 193.010$ amuA ²
$C = 1789.84 \pm 0.20$ Mc/sec	$I_{c, \text{eff}} = 282.445$ amuA ²
$\kappa = -0.57035 \pm 0.00005$	
$\Delta = -0.032 \pm 0.020$ amuA ²	

The expected planarity of the molecule was confirmed by the smallness of the inertia defect Δ ($= I_{c, \text{eff}} - I_{a, \text{eff}} - I_{b, \text{eff}}$) $= -0.03$ amuA². The negative value of Δ will be discussed in § 4.

§ 3. Internal Rotation

Either of the two groups in a phenol molecule rotation relative to each other is asymmetric with respect to the axis of internal

rotation (a -axis). Such a case was treated theoretically by Burkhard³⁾ with very complicated results. Since the moment of inertia of the OH-group about the a -axis is very small in comparison with that of the C_6H_5 -group, the moments of inertia of the whole molecule are almost indifferent to the torsional angle between the two groups. If we assume that the OH-group is symmetric and the hindering potential is represented by the equation $V = (V_2/2)(1 - \cos 2x)$, the usual treatment on the internal rotation will be applicable to this molecule.

The equation which describes the internal rotation is

$$\frac{d^2M}{dx^2} + \frac{2I_1I_2}{I_a\hbar^2} \left[W - \frac{V_2}{2}(1 - \cos 2x) \right] M = 0 \quad (1)$$

where W is the energy of the internal rotation and I_1 and I_2 are the moments of inertia of the OH-group and the C_6H_5 -group respectively, about the a -axis, and I_a is related with $I_a = I_1 + I_2$.

The solution of the equation (1) can be expressed by

$$M(x) = e^{i\sigma x} P(x)$$

where $\sigma = -(I_1/I_a)K$, and $P(x)$ is expanded in the Fourier series

$$P(x) = \sum_{m=-\infty}^{\infty} a_m e^{imx}$$

We have two types of solutions which are designated by $\tau=1$ and $\tau=2$ according as $m = (\dots, -4, -2, 0, 2, 4, \dots)$ and $m = (\dots, -3, -1, 1, 3, \dots)$, respectively, in the similar way as used in the treatment of methyl alcohol by Dennison and others⁴⁾.

When the potential barrier is relatively high, the internal rotation energy $W_{K\tau n}$ is expressed in good approximation by⁵⁾

$$W_{K1n} = \alpha_n - \frac{\beta_n}{2} \cos \frac{\pi I_1}{I_a} K$$

$$W_{K2n} = \alpha_n + \frac{\beta_n}{2} \cos \frac{\pi I_1}{I_a} K$$

where α_n is the n -th torsional energy in the high barrier limit. Since the value of I_1/I_a of phenol is so small being of the order of 0.01 that W_{K1n} and W_{K2n} are very close to $\alpha_n - \beta_n/2$ and $\alpha_n + \beta_n/2$ respectively when K is small. The selection rule of b -type transition is ΔK (or $\Delta K_{-1}) = \pm 1$ and $\tau = 1 \rightarrow 2$. Thus the splitting of doublet lines which is caused by the internal rotation should be nearly equal

to $2\beta_n$. From the observed splittings in the ground torsional state, the potential barrier height was calculated to be 1100 cm^{-1} for the assumed value of $I_1 = 0.80 \text{ amu}\text{\AA}^2$.

§ 4. Inertia Defect

We shall consider the effect of internal rotation on the effective moments of inertia. Two of the geometrical moments of inertia of the whole molecule, I_b and I_c , are given by the functions of the torsional angle, x , between the two groups, while the other moment of inertia, I_a , is independent of x . The approximate expressions are

$$I_a = I_a^{(0)}$$

$$I_b = I_b^{(0)} + I_1 \sin^2 x$$

$$I_c = I_c^{(0)} - I_1 \sin^2 x$$

where $I_a^{(0)}$, $I_b^{(0)}$ and $I_c^{(0)}$ are the moments of inertia when the OH-group is in the plane comprising the C_6H_5 -group. The effective moments of inertia and the rotational constants are given by

$$A = \frac{h}{8\pi^2} \frac{1}{I_{a,\text{eff}}}, \quad I_{a,\text{eff}} = I_a^{(0)}$$

$$B = \frac{h}{8\pi^2} \frac{1}{I_{b,\text{eff}}} = \frac{h}{8\pi^2} \left\langle \frac{1}{I_b} \right\rangle_{av}$$

$$C = \frac{h}{8\pi^2} \frac{1}{I_{c,\text{eff}}} = \frac{h}{8\pi^2} \left\langle \frac{1}{I_c} \right\rangle_{av}$$

where the average is carried out for the torsional state obtained in the previous section.

The inertia defect is expressed in the form:

$$\begin{aligned} \Delta &= I_{c,\text{eff}} - I_{a,\text{eff}} - I_{b,\text{eff}} \\ &= I_c^{(0)} - I_a^{(0)} - I_b^{(0)} + \delta \end{aligned}$$

where δ represents the effect of internal rotation on the inertia defect. The value of δ is estimated to be $-0.11 \text{ amu}\text{\AA}^2$ for the barrier height of $V_2 = 1100 \text{ cm}^{-1}$.

Since the value of Δ obtained in § 2 is $-0.03 \text{ amu}\text{\AA}^2$, the value of $(\Delta - \delta) = (I_c^{(0)} - I_a^{(0)} - I_b^{(0)})$ is found to be $0.08 \text{ amu}\text{\AA}^2$. This can be compared with the values of inertia defect of $C_5H_5N^{7)}$, $C_6H_5F^{8)}$ and $C_6H_5CN^{9)}$, which are 0.0336 , 0.027 and $0.073 \text{ amu}\text{\AA}^2$, respectively. The effect of the stretching and tipping vibrations of the OH-bond on the inertia defect is considered to be small¹⁰⁾.

§ 5. Conclusion

The effective moments of inertia of a phenol molecule was obtained by the use of a rigid rotor model. From the inertia defect, this

molecule was shown to be planar in its equilibrium configuration. The negative value of the quantum defect was considered to be caused by the internal rotation of the OH-group. The potential barrier hindering the internal rotation was determined to be $V_2=1100\pm100\text{ cm}^{-1}$ on the assumption that the potential barrier was represented by $V=(V_2/2)(1-\cos 2x)$. The relatively high barrier and the planarity may be explained as due to the double bond character of the CO-bond which arises from the conjugation¹¹⁾ between the π -electrons of the benzene ring and the lone-pair electrons of the oxygen atom.

Acknowledgement

I wish to express my hearty thanks to Prof. K. Shimoda for his guidance and advice throughout this work. My thanks are also due to Dr. T. Nishikawa and Mr. T. Oka for their valuable discussions.

References

- 1) Summary; C. C. Lin and J. D. Swalen: Rev. Mod. Phys., to be published. C. H. Townes and A. L. Schawlow: *Microwave Spectroscopy* (Mc Graw-Hill, 1955).
- 2) E. N. Lassettree and L. B. Dean Jr.: J. Chem. Phys. **17** (1949) 317.
- 3) D. G. Burkhard: J. Chem. Phys. **21** (1953) 1541.
- 4) J. S. Koehler and D. M. Dennison: Phys. Rev. **57** (1940) 1006. D. G. Burkhard and D. M. Dennison: Phys. Rev. **84** (1951) 408. E. V. Ivash and D. M. Dennison: J. Chem. Phys. **21** (1953) 1064.
- 5) K. T. Hecht and D. M. Dennison: J. Chem. Phys. **26** (1957) 31.
- 6) B. T. Darling and D. M. Dennison: Phys. Rev. **57** (1940) 128. C. C. Costain: J. Chem. Phys. **29** (1958) 864.
- 7) B. Bak, L. Hansen-Nygaard and J. Restrup-Andersen: J. Mol. Spect. **2** (1958) 361.
- 8) B. Bak, D. Christensen, L. Hansen-Nygaard and E. Tannenbaum: J. Chem. Phys. **26** (1957) 134.
- 9) D. R. Lide, Jr.: J. Chem. Phys. **22** (1954) 1577.
- 10) V. W. Laurie: J. Chem. Phys. **28** (1958) 704.
- 11) C. A. Coulson: *Valency* (Oxford Univ. Press, 1953).

Zeeman Effect of Nuclear Quadrupole Resonance Spectrum in 1, 3, 5-Trichlorobenzene

By Yonezo MORINO and Masaharu TOYAMA

*Department of Chemistry, Faculty of Science,
University of Tokyo, Tokyo*

(Received November 10, 1959)

A study of the Cl^{35} resonance spectrum was carried out at the room temperature on a single crystal of 1, 3, 5-trichlorobenzene. Spatial orientation of the C-Cl bonds was determined to the accuracy of 1° . An orthorhombic structure was concluded, with the unit cell containing at least four equivalent molecules oriented with the symmetry of D_{2h} . The angles between the C-Cl bonds in each molecule were close to the hexagonal angle, but one of the C-Cl bonds was deformed by ca. 1.6° from the plane of the other two. The asymmetry parameters were observed to be 0.09₃, 0.11₁, and 0.12₉ for three absorption lines, 35.020 Mc, 35.296 Mc, and 35.545 Mc, respectively. The results were discussed from the viewpoint of intermolecular interaction.

§ 1. Introduction

In the preceding Zeeman studies^{1,2)} the asymmetry parameters of the electric field gradient at the Cl^{35} nuclei in cyanuryl chloride were observed, which were very large ($\eta = 0.23$ and 0.26) compared with that in *p*-dichlorobenzene ($\eta = 0.08$).³⁾ This large asymmetry was concluded to originate from large electronegativity of nitrogen atoms in the triazine ring. In cyanuryl chloride lone-pair electrons on chlorine atoms are attracted towards the ring so strongly that the double bond character of the C-Cl bonds is more increased than those in chlorine derivatives of benzene. This conclusion will be confirmed by the measurement on 1, 3, 5-trichlorobenzene, which may be quite similar to cyanuryl chloride in its ring structure.

1, 3, 5-Trichlorobenzene is also interesting in its molecular structure. Bastiansen and Hassel⁴⁾ have reported from the studies of electron diffraction by gaseous molecules that the observed interatomic distances of hexachlorobenzene were best explained by assuming a bending of the C-Cl bonds of about 15° out of plane of benzene ring, and those of 1, 2, 3, 5-tetrabromobenzene by assuming a bending of about 12° of the C-Br bonds. These results are of so fundamental importance in structural chemistry that they should be studied further. The measurement of the Zeeman effect of the nuclear quadrupole resonance spectrum is also most suitable for

this purpose, since the principal *z*-axis of the field gradient at the Cl nucleus must be along the C-Cl bond direction. In 1, 3, 5-trichlorobenzene the ortho steric hindrance may be small so that three C-Cl bonds are expected to lie in the benzene plane. Thus the measurement of the bond angles in this molecule will give a fundamental basis for the further studies of the planarity of the substituted benzene molecules. No structural investigation has been made for this molecule.

Three Cl^{35} resonance lines with equal intensities have been observed in 1, 3, 5-trichlorobenzene by Bray, et al.⁵⁾ This result indicates that the crystal of 1, 3, 5-trichlorobenzene contains three groups of chemically inequivalent lattice sites,* and each of the groups includes the same number of chlorine atoms. Since a molecule contains only three Cl atoms, it allows two cases for the probable crystalline structure; (1) all the molecules occupy the equivalent positions in a crystal, whereas three Cl atoms in a molecule are inequivalent, or (2) three Cl atoms in a molecule are equivalent, whereas a unit cell contains three sorts of inequivalent molecules with equal amount.

For the location of the principal axes of the

* The terms "physically" and "chemically" equivalent were introduced by Das and Hahn (Nuclear Quadrupole Resonance spectroscopy in Solid State Physics, Supplement I, Academic Press Inc., New York (1958) Sec. 1e).

field gradients and for the determination of the asymmetry parameters, a number of methods of Zeeman study have been proposed, of which the most popular one is a method of the measurement of no-splitting loci.⁽⁶⁾⁻⁸⁾ This method is excellent in giving the precise direction of the z -axis, but it is not convenient for determining other axes and the asymmetry parameter. The asymmetry parameter is precisely determined from the splitting by a static magnetic field applied parallel to the principal xy -plane, where the splitting due to the non-axial field gradient is very large if a strong magnetic field is applied.

A theoretical calculation⁹⁾ suggested that the directions of the principal x - and y -axes may precisely be determined by measuring the dependence of the relative intensity of the Zeeman components upon the direction of the rf field. When a static magnetic field is applied parallel to the xy -plane and the rf field in the direction not close to the z -axis, the relative intensity P_r for the spin $I=3/2$ is given to the first order in η as follows:

$$P_r = \frac{P(-)}{P(+) + P(-)} = \frac{1}{1 + (1 + 4/3 \cdot \eta) \cot^2 \varphi_r}, \quad (1)$$

where $P(+)$ and $P(-)$ denote the intensities of the inner and the outer pairs of Zeeman components, respectively, and (θ_r, φ_r) the direction of the rf field in regard to the principal axes. Hence the inner or the outer pair disappears, depending upon whether the direction of the rf field is parallel to the yz -plane ($\varphi_r=90^\circ$) or to the xz -plane ($\varphi_r=0^\circ$). In the present study this new method was employed together with the above two methods.

§ 2. Experimental and Results

The apparatus for the Zeeman study was described in the preceding paper.¹⁾ A super-regenerative spectrometer^{(10), (11)} was used for the observation of absorption lines, which were displayed on a recorder at the room temperature. The relative intensity of the Zeeman components was calculated from the ratio of the peak-to-peak deflections in the derivative of absorption lines. Since the energy absorbed in the nuclear quadrupole resonance is small compared with the total energy of the rf field, the deflection, i.e., the voltage change

in the rf coil, is approximately proportional to the absorbed energy, in such a narrow frequency range used for the Zeeman effect. The static magnetic field actually applied was ca. 30 gauss in its strength for the ordinary observation, and ca. 100 gauss when necessary.

Commercial 1, 3, 5-trichlorobenzene supplied by Tokyo Chemical Industry Co. Ltd was purified by recrystallization from alcoholic solution which was decolorized through a layer of active charcoal. A single crystal of about 10 g was grown from the molten state.

Table I. Cl^{35} Nuclear quadrupole resonance frequencies in 1,3,5-trichlorobenzene.

Temperature	Absorption lines		
	$\nu_a(\text{Mc})$	$\nu_b(\text{Mc})$	$\nu_o(\text{Mc})$
77° K	35.543	35.893	36.112
195° K	35.305*	35.620*	35.856*
299° K	35.020	35.296	35.545

* First observed in the present experiment.

The three pure quadrupole absorption lines will be designated as ν_a , ν_b , and ν_o , in order of the frequency increase, and are reproduced in Table I. When a static magnetic field was applied, two lower absorption lines ν_a and ν_b split in general into about sixteen lines, while the highest one ν_o into about eight. This shows that ν_a and ν_b come from four sorts of physically inequivalent q -tensors a_1 , a_2 , a_3 , and a_4 , and b_1 , b_2 , b_3 , and b_4 , respectively, while ν_o from two $c_{1,2}$ and $c_{3,4}$. The splittings were all symmetric with respect to three orthogonal axes X , Y , and Z taken in the crystal and to the planes XY , YZ , and ZX ; viz., the spatial pattern of the Zeeman splitting was of the symmetry of D_{2h} . Hereafter the axes designated by capital letters will represent the crystal-fixed ones while those by small letters the bond-fixed ones. Any direction will be expressed by direction cosines in regard to the above crystal-fixed axes without referring to it.

By the restriction due to the construction of the magnet¹⁾ the detailed observation had to be confined to a range of about 40° around the Z -axis. The results are illustrated in Fig. 1. In this diagram the polar coordinates (θ, φ) denote space-fixed ones used for the experiment, which are projected on a horizontal plane from the origin taken at the

center of the sample. This projection is convenient, because the directions in a great circle are projected into a straight line. In fact, the projections of the xy -planes are represented by straight lines in Fig. 1. They were determined through location of the directions in which the relative splitting defined by $\Delta\nu_+/\Delta\nu_-$ became maximum, where $\Delta\nu_+$ and $\Delta\nu_-$ denote the splittings of the inner and the outer pairs, respectively. On the other hand no-splitting loci are expressed by circular lines. The direction of the rf field was set to be vertical, that is, in the polar direction in Fig. 1 which was transformed into the crystal-fixed coordinates to be $(-0.054, 0.040, 0.998)$.

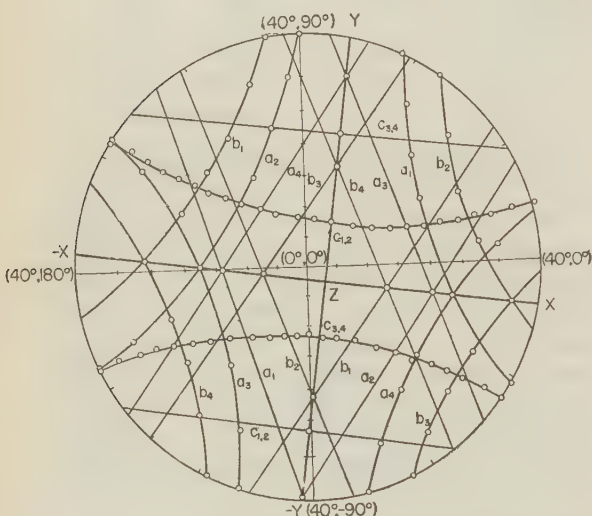


Fig. 1. Spatial pattern of the Zeeman splittings around the Z -axis. (θ, φ) denotes the polar coordinates actually used in the experiment, which are projected onto a horizontal plane from the origin taken at the center of the sample. The straight lines designated by a_1, b_1 , etc. represent the projections of the principal xy -planes of a_1, b_1 , etc. while the circular lines those of no-splitting loci.

The asymmetry parameters and the directions of the principal x - and y -axes were determined from the relative splittings and the relative intensities of the Zeeman components in the directions parallel to the xy -plane. The directions of the principal z -axes were first roughly determined to be perpendicular to the xy -planes determined above. Then the z -axes were refined through application of the method of least squares to the

no-splitting loci. The refined asymmetry parameters and directions of the x -axes were obtained from the observation in the xy -plane thus corrected. This process was repeated untill the deviation became smaller than the probable errors. Special attention was payed to keep good convergence, referred to the theoretical requirement that, the closer to the xy -plane, the larger the relative splitting should be.

Table II. Directions of the principal z -axes (C-Cl bond directions).

z -Axes	X	Y	Z
a_1	0.864 ₆	0.423 ₄	0.270 ₅
a_2	-0.862 ₄	0.426 ₇	0.272 ₅
a_3	-0.864 ₆	-0.424 ₂	0.269 ₃
a_4	0.867 ₁	-0.418 ₁	0.270 ₈
b_1	-0.862 ₂	0.482 ₀	0.156 ₀
b_2	0.871 ₃	0.464 ₀	0.160 ₁
b_3	0.864 ₅	-0.476 ₅	0.160 ₁
b_4	-0.865 ₄	-0.475 ₂	0.159 ₃
c_1, c_2	-0.005 ₈	-0.915 ₁	-0.403 ₂
c_3, c_4	-0.010 ₀	0.912 ₀	-0.410 ₁

Table III. Average directions of the principal axes of the field gradient and the normal to the benzene ring.

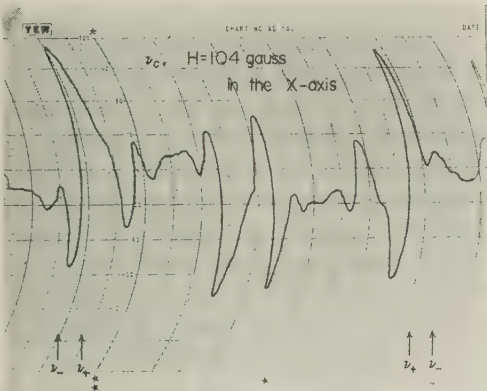
	X	Y	Z
z -Axes:			
$\bar{a}$	0.864 ₇	0.423 ₁	0.270 ₈
$\bar{b}$	-0.865 ₉	0.474 ₄	0.158 ₉
$\bar{c}$	-0.007 ₉	-0.913 ₅	-0.406 ₇
x -Axes:			
$\bar{a}$	-0.07 ₇	-0.42 ₁	0.90 ₄
$\bar{b}$	-0.02 ₉	-0.36 ₅	0.93 ₀
$\bar{c}$	-0.07 ₂	-0.40 ₅	0.91 ₁
Normal	-0.071 ₀	-0.413 ₇	0.907 ₆

The final directions of the principal z -axes are tabulated in Table II. They are symmetric with respect to the axes X, Y , and Z , and to the planes XY, YZ , and ZY . The average directions of the z -axes are, therefore, calculated by a symmetry transformation of all the q -tensors into the position of those designated by suffix 1. They are listed in Table III together with the average directions of the x -axes, which were determined by Eq. (1) from the relative intensities shown in

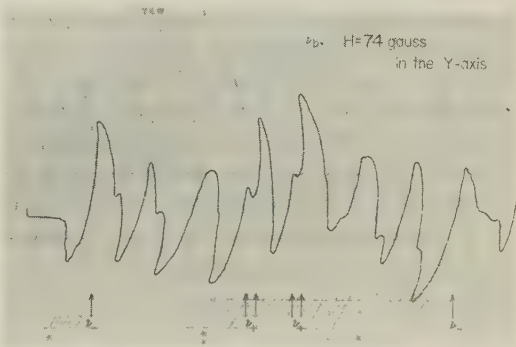
Table IV. Zeeman effect by a magnetic field applied parallel to the principal *xy*-plane, where (*a_i*, *a_j*) designates the intersection between the *xy*-planes of the *q*-tensors *a_i* and *a_j*.

Directions	Magnetic field (gauss)	Relative splitting	Relative intensity	Asymmetry parameter
<i>v_a</i>				
(<i>a</i> ₁ , <i>a</i> ₂)	113	0.909±0.007	0.05 ₆ ±0.07	0.09 ₁ ±0.01
(<i>a</i> ₃ , <i>a</i> ₄)	148	0.895 "	0.11 ₁ "	0.10 ₅ "
(<i>a</i> ₁ , <i>a</i> ₄)	112	0.909 "	0.13 ₅ "	0.09 ₃ "
(<i>a</i> ₂ , <i>a</i> ₃)	118	0.910 "	0.11 ₇ "	0.09 ₀ "
<i>v_b</i>				
(<i>b</i> ₁ , <i>b</i> ₂)	106	0.893±0.007	0.09 ₁ ±0.07	0.10 ₇ ±0.01
(<i>b</i> ₃ , <i>b</i> ₄)	98	0.884 "	0.08 ₈ "	0.11 ₄ "
(<i>b</i> ₁ , <i>b</i> ₄)	101	0.890 "	0.09 ₃ "	0.11 ₂ "
(<i>b</i> ₂ , <i>b</i> ₃)	99	0.894 "	0.12 ₇ "	0.10 ₉ "
<i>v_c</i>				
(<i>c</i> ₁ , <i>c</i> ₂)*	107	unobservable	0.00	—
(<i>c</i> ₃ , <i>c</i> ₄)*	107	(0.882)	<0.02	(0.12)

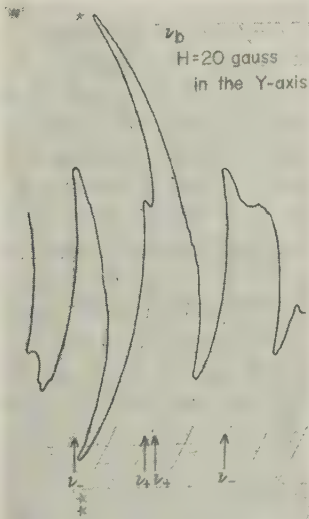
* Intersection with the *YZ*-plane.



(a)



(b-1)



(b-2)

Fig. 2. Typical charts of Zeeman splittings. The complicated feature was brought about by overlapping of the sidebands owing to super-regeneration. (a) The splitting of *v_c* in the *X*-axis. (b-1) The splitting of *v_b* in the *Y*-axis, which was further split by increasing the strength of magnetic field (see (b-2)).

Table IV, referred to the curvatures of the no-splitting loci.

The relative splitting and the relative intensity in Table IV were observed in the direction of the intersection between two principal *xy*-planes of each pair of chemically equivalent *q*-tensors, such as (*a*₁, *a*₂) and (*a*₃, *a*₄). According to the symmetric orientation of the *q*-tensors, the intersection lies in the plane *XY*, *YZ*, or *ZX*, so that the splitting lines coalesce into eight lines. In this observation a large magnetic field was applied,

and the splitting could be measured fairly accurately, but the intensity may contain considerable error (± 0.07) due to overlapping of the side bands owing to super-regeneration. The asymmetry parameters were calculated from these splittings as listed in Table IV.

In the above observation the direction of the rf field was set to be nearly parallel to the xz -plane of $c_{1,2}$ and $c_{3,4}$, and the outer pair of Zeeman components of ν_c was hardly observed when the magnetic field was applied parallel to the xy -plane. The asymmetry parameter of c , therefore, could not accurately be determined from the splittings in these directions. A more precise value was obtained from the observation in the direction of the X -axis. Although this direction is parallel to the xy -plane of c and close to the y -axis as is easily seen from Table III, the outer pair was still distinctly observed with considerable intensity as if the z -axis were deviated from the YZ -plane (see Fig. 2(a) and Table V). The asymmetry parameter η_c and the apparent deviation $\Delta\theta_c$ are obtained below from the diagram in Fig. 3, which illustrates the relation of the splitting and the intensity with the direction of the magnetic field for various asymmetry parameters in the case of the rf field applied parallel to the yz -plane:⁹⁾

$$\eta_c = 0.129 \pm 0.02,$$

$$\Delta\theta_c = 1.3^\circ \pm 0.3^\circ.$$

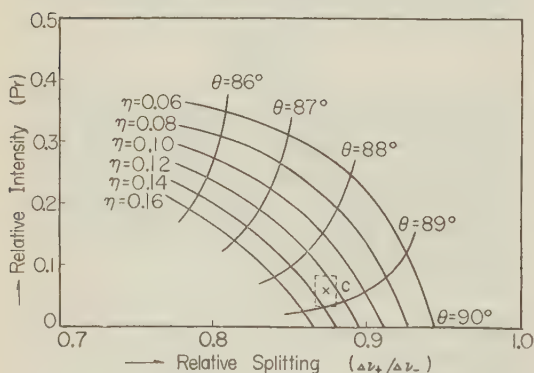


Fig. 3. The relation of the splitting and the intensity with the asymmetry parameter and the direction of the magnetic field, where the rf field is applied parallel to the xz -plane (not close to the z -axis) and the magnetic field parallel to the yz -plane, θ denoting the angle between the directions of the magnetic field and the z -axis. The observed values of ν_c in the X -axis are plotted at the point c with the range of errors.

In the directions of the X , Y , and Z axes, the absorption lines split into four lines so long as the applied magnetic field was weak. When the strength of the field increased, however, each inner component of ν_a and ν_b split further into two with the same intensities in the direction of the Y -axis (Fig. 2(b)) and showed a tendency to broaden out in the X -axis, whereas it did not split further in the Z -axis. The fine splitting δ_+ of each inner component is listed in Table V as a ratio to the splitting of the outer pair, $\delta_+/\Delta\nu_-$.

Since there is no possibility of a superlattice,* these phenomena, together with the apparent deviation of c from the YZ -plane, suggest that the crystal may be a twin crystal consisting of two species slightly rotated about the Z -axis. The phase difference between them is estimated from the above results to be as follows:

$$2.6^\circ \pm 0.5^\circ \text{ from } \nu_a \text{ in the } Y\text{-axis,}$$

$$2.7^\circ \pm 0.5^\circ \text{ from } \nu_b \text{ in the } Y\text{-axis,}$$

$$2.9^\circ \pm 0.7^\circ \text{ from } \nu_c \text{ in the } X\text{-axis,}$$

and $2.7^\circ \pm 0.5^\circ$ on the average. The twinning plane may be parallel to the YZ -plane or to the XZ -plane, and coincides with the contact plane of two species. The twinning axis may be assigned to the X - or Y -axis.

The fine splitting was not resolved up to about 150 gauss in the detailed observation around the Z -axis as shown in Fig. 1 and Table IV. Furthermore, in the direction fairly deviated from the Z -axis the fine splitting was hardly measurable because of complexity in the spectrum. Then it should be noted here that Tables II and III indicate the results for the average of two species, which may agree with those for one species in the present case, since the phase difference is sufficiently small. Hence in the discussion of the following section let the axes X , Y , and Z represent the symmetry axes for one species. The splittings and the intensities in the directions of these axes calculated from the above results are in good agreement with the observed ones (see Table V).

* If it be composed of a superlattice, the crystal should contain eight molecules in a unit cell which are chemically equivalent but physically inequivalent to one another. Such a lattice is impossible to exist in this crystal, because the crystalline symmetry is orthorhombic as derived in the following section.

Table V. Zeeman effect by a magnetic field applied parallel to the symmetry axes X , Y , and Z .

Absorption lines	Magnetic field (gauss)	Relative splitting		Relative intensity		Fine splitting
		obs.	calc.	obs.	calc.	
X-axis						
ν_a	41	0.310 ± 0.007	0.313	$0.18_3 \pm 0.05$	0.18	broad
ν_b	41	0.302 "	0.312	0.19_9 "	0.18	broad
ν_c	104	0.874 "	0.885	$0.05_8 \pm 0.03$	0.02	
Y-axis						
ν_a	84	$0.199 \pm 0.007^*$	0.200*	$0.42_0 \pm 0.05$	0.32	0.051
ν_b	74	0.116 " *	0.136*	0.35_8 "	0.35	0.052
ν_c	42	0.385 "	0.396	0.14_2 "	0.09	
Z-axis						
ν_a	79	0.390 ± 0.007	0.394	$0.42_0 \pm 0.05$	0.39	
ν_b	79	0.608 "	0.592	0.41_5 "	0.39	
ν_c	36	0.182 "	0.179	0.40_7 "	0.37	

* Average values of two fine splitting lines.

§ 3. Discussion

(1) Crystalline and molecular structure

If it is assumed that the principal z -axis lies along the C-Cl bond, and that the angles between the C-Cl bonds in each molecule are close to the hexagonal angle, the crystalline structure of 1, 3, 5-trichlorobenzene is concluded from the results in Table II to correspond to the case (1) proposed in the Introduction. The crystal contains at least four molecules in a unit cell which are chemically equivalent but physically inequivalent, that is, equivalent except for orientations. The suffixes 1, 2, 3, and 4 added to the q -tensors in the above analysis designate these four molecules, while a , b , and c three Cl atoms in each molecule which are inequivalent in the crystal. The orientation of molecules is symmetric with respect to the planes XY , YZ , and ZX as shown in Fig. 4. The bond c in each molecule is parallel to the YZ -plane, while the other two are oblique with respect to all the symmetry axes X , Y , and Z . The direction normal to the benzene plane is estimated from the directions of three C-Cl bonds as listed in Table III. The normal direction is slightly inclined to the YZ -plane. Since the molecule has no symmetry in the crystal, it is impossible to occupy any position on the symmetry elements except a screw axis and a glide plane.

The relation between the crystalline symmetry and the pattern of the Zeeman splitting has comprehensively been studied by Shimo-

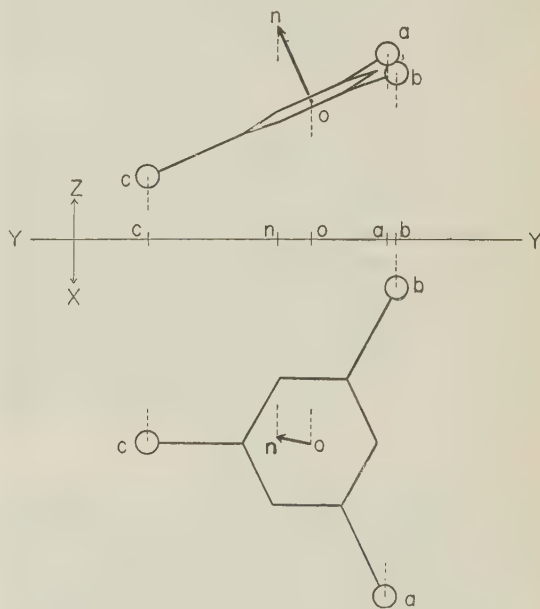


Fig. 4. Orientation of a molecule in the crystalline 1, 3, 5-trichlorobenzene, the upper half showing the projection on the YZ -plane and the lower half on the XZ -plane. The vector n denotes the normal to the benzene ring. Other three molecules in a unit cell are located in the orientations transformed symmetrically with respect to the XY , YZ , or/and ZX planes.

mura.¹²⁾ The same analysis being applied to 1, 3, 5-trichlorobenzene, its crystalline symmetry is concluded to be orthorhombic, since the Zeeman pattern has the symmetry of D_{2h} . Cubic, tetragonal, and hexagonal symmetries are excluded, because they are

Table VI. Angles between the three C-Cl bonds in each molecule.

Bonds	Molecules				Average
	1	2	3	4	
<i>a</i> , <i>b</i>	119.9°	120.7°	120.1°	120.6°	120.3°
<i>b</i> , <i>c</i>	119.9°	119.6°	120.6°	119.3°	119.9°
<i>c</i> , <i>a</i>	120.1°	119.7°	119.3°	120.1°	119.8°
Out-of-plane deformation*	+1.5°	-2.1°	+1.2°	-1.5°	+1.6°

(The error; $\pm 1^\circ$)

* Deviation of the bond *c* from the plane formed by the bonds *a* and *b*, the positive sign denoting the direction of the vector product $\mathbf{a} \times \mathbf{b}$.

higher symmetries than D_{2h} . On the other hand, triclinic symmetry is excluded, because of lack of symmetry. The crystal with monoclinic symmetry may accidentally give a Zeeman pattern with the symmetry of D_{2h} as observed in cyanuryl chloride,¹¹ but in this case a unit cell cannot contain such four molecules as described above. Hence monoclinic symmetry is also excluded.

Three crystalline axes are parallel to the axes *X*, *Y*, and *Z*, of which the *Z*-axis seems to be parallel to the shortest crystalline axis, because the single crystal was grown along it. The molecular normal makes an angle, 24.8°, with the shortest axis. Schnepf¹³ has, however, estimated from the measurement of the near ultraviolet spectrum at 4.2°K that the normal made an angle of about 20° with the long axis. Both results are in good agreement except for the assignment of the crystalline axes.

The angles between the C-Cl bonds in each molecule agree with the hexagonal angle, 120°, within the errors as shown in Table VI, but the three C-Cl bonds are not coplanar. Really a C-Cl bond was found to be inclined by ca. 1.6° to the plane formed by the other two. This inclination corresponds to the deformation of 0.8° of the C-Cl bonds, if it is assumed that the three C-Cl bonds are deformed by the same angle out of the benzene plane. The deformed molecules are so arranged in a crystal as to satisfy the symmetry requirement that four molecules in a unit cell are transformed from one molecule to others by the symmetry operation belonging to D_{2h} ; in other words, the out-of-plane deformation takes place symmetrically to the planes *XY*, *YZ*, and *ZX*.

The deviation obtained above are compa-

table with the probable error of the experiment, $\pm 1^\circ$, but the existence of the out-of-plane deformation must be admitted, because otherwise the deformation could not take place only in the direction satisfying the symmetry requirement.

There may be a doubt that the molecule keeps rigorously the planar form and the apparent deformation comes from the fact that the principal *z*-axis of the field gradient is off from the C-Cl bond axis. In this connection it should be worth while to mention that the *z*-axis of the field gradient at the bromine nucleus in propargyl bromide exactly coincides with the C-Br bond.¹⁴ In addition, in 1, 2, 4, 5-tetrachlorobenzene,¹⁵ the angle between two ortho C-Cl bonds has been estimated to be $63.5^\circ \pm 1^\circ$ from the Zeeman study, and observed to be 64.5° by the study of X-ray diffraction.

It is likely that the deformation of the bond angle is brought about by the intermolecular interaction due to the neighboring molecules in the crystal and the intramolecular steric repulsion due to the atoms at the ortho positions. In 1, 3, 5-trichlorobenzene the latter effect may be small, because the sum of van der Waals radii of hydrogen and chlorine atoms is smaller than the interatomic distance estimated from the atomic radii. On the other hand, the intermolecular interaction is supposed to be considerably strong; the resonance frequencies due to three Cl^{35} nuclei, which should be equivalent in the free molecule, are distributed in the crystal over a considerably wide range (600 kc) compared with other derivatives of benzene (300 kc).⁵ Still the intermolecular interaction scarcely affects the C-Cl bond angles in the benzene derivatives as was observed at the present experiment. It makes

a contrast against the case of γ -BHC; in the latter molecule the bond angles are strongly deformed by the intermolecular interaction as was obtained by the X-ray diffraction¹⁶⁾ and by the nuclear quadrupole resonance spectra.¹⁷⁾⁻¹⁹⁾

This result gives a fundamental basis for the further studies of planarity of substituted benzene molecules, because it suggests that the contribution of intermolecular interaction may be neglected when the ortho steric repulsion between heavy atoms such as chlorine takes part in the deformation of bond angles.

(2) Nature of the C-Cl bonds

The quadrupole coupling constant and the asymmetry parameter increase in the sequence of *a*, *b*, and *c*. It is well interpreted in terms of intermolecular induction effect. Since the Cl atom in a C-Cl bond carries negative charges, the electron on the Cl atom may be repelled towards the benzene ring, when two Cl atoms are adjacent in the crystal. If the σ -electrons are repelled, the ionic character of the C-Cl bond decreases, whereas, if the π -electrons are repelled, the double bond character increases. The decrease in ionic character increases the absolute value of coupling constant and the increase in double bond character decreases it. However, the effect of ionic character upon the coupling constant is stronger than that of double bond character. Thus the intermolecular induction increases the absolute value of coupling constant as a whole. On the other hand the increase in double bond character increases the asymmetry parameter, but the change in ionic character scarcely affects it. Hence the intermolecular induction increases the asymmetry parameter. From the results

Table VII. Nature of the C-Cl bonds.

	<i>a</i>	<i>b</i>	<i>c</i>
Coupling constant (Mc)*			
	71.1 ₂	71.8 ₃	72.2 ₈
Asymmetry parameter			
	0.09 ₃ ±0.01	0.11 ₁ ±0.01	0.12 ₉ ±0.02
Double bond character			
	0.03 ₃	0.04 ₂	0.04 ₉
Ionic character			
	0.21 ₈	0.20 ₈	0.19 ₉

* The values at 0°K estimated by extrapolation.

mentioned above it is concluded that the induction effect increases in the order of *a*, *b*, and *c* in 1, 3, 5-trichlorobenzene. The ionic and the double bond characters of the three C-Cl bonds are calculated by Townes-Dailey's method.²⁰⁾⁻²²⁾ The results are shown in Table VII.

The asymmetry parameter of 1, 3, 5-trichlorobenzene obtained above is far smaller than that of cyanuryl chloride as it was expected. This result supports the preceding conclusion¹⁾ that in cyanuryl chloride lone-pair electrons on chlorine atoms are strongly attracted towards the triazine ring in consequence of large electronegativity of nitrogen atoms. The comparison is also made with that of *p*-dichlorobenzene ($\eta=0.08$)³⁾ and 1, 2, 4, 5-tetrachlorobenzene ($\eta=0.125$)¹⁵⁾; the asymmetry parameter of 1, 3, 5-trichlorobenzene is intermediate between them. It suggests that the resonance effect to π -electrons on the C-Cl bond decreases in the order of ortho, meta, and para positions.

Finally it should be noted that the *p*-orbit perpendicular to the benzene ring forms a π -bond in this molecule, as is easily seen from the fact that the direction of the principal *x*-axis agrees with the molecular normal within the experimental error ($\pm 8^\circ$) as shown in Table III.

In conclusion, the authors wish to thank the Ministry of Education of Japan for aid in this investigation.

References

- 1) Y. Morino, T. Chiba, T. Shimozawa and M. Toyama: J. Phys. Soc. Japan **13** (1958) 869.
- 2) F. J. Adrian: J. Chem. Phys. **29** (1958) 1381.
- 3) C. Dean: Phys. Rev. **86** (1952) 607.
- 4) O. Bastiansen and O. Hassel: Acta Chem. Scand. **1** (1947) 489.
- 5) P. J. Bray, R. G. Barnes and R. Bersohn: J. Chem. Phys. **25** (1956) 813.
- 6) H. C. Meal: J. Chem. Phys. **24** (1956) 1011.
- 7) C. Dean: Phys. Rev. **96** (1954) 1053.
- 8) K. Shimomura: J. Phys. Soc. Japan **12** (1957) 657.
- 9) M. Toyama: J. Phys. Soc. Japan **14** (1959) 1727.
- 10) R. V. Pound and W. D. Knight: Rev. Sci. Instr. **21** (1950) 152.
- 11) C. Dean: Thesis, Harvard University (1952).
- 12) K. Shimomura: J. Phys. Soc. Japan **12** (1957) 652.
- 13) O. Schnepf: J. Chem. Phys. **30** (1959) 863.

- 14) Y. Kikuchi, E. Hirota and Y. Morino: J. Chem. Phys. **31** (1959) 1139.
- 15) C. Dean, M. Pollak, B. M. Craven and G. A. Jeffrey: Acta Cryst. **11** (1958) 710.
- 16) G. W. van Vloten, Ch. A. Kruissink, B. Strijk and J. M. Bijvoet: Acta Cryst. **3** (1950) 139.
- 17) Y. Morino, I. Miyagawa, T. Chiba and T. Shimozawa: J. Chem. Phys. **25** (1956) 185.
- 18) J. Duchesne, A. Monfils and J. Depireux: Compt. rend. **243** (1956) 144.
- 19) Y. Morino, T. Chiba, T. Shimozawa, M. Toyama and K. Ito: Rev. Univ. des Mines 9^e Sér. T. XV (1959) 591.
- 20) C. H. Townes and B. P. Dailey: J. Chem. Phys. **17** (1949) 783.
- 21) C. H. Townes and A. L. Shawlow: *Microwave Spectroscopy* (McGraw-Hill Inc., New York 1955) 237.
- 22) R. Bersohn: J. Chem. Phys. **22** (1954) 2078; see also the reference 1.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 2, FEBRUARY, 1960

Microwave Spectrum of Ethyl Iodide, I.

By Takahiro KASUYA and Takeshi OKA

*Department of Physics, Faculty of Science,
University of Tokyo, Tokyo*

(Received September 17, 1959)

Microwave spectrum of ethyl iodide molecule C_2H_5I was studied. The obtained rotational constants are: $A=29106.2 \pm 0.5$ Mc/sec, $B=2979.2 \pm 0.1$ Mc/sec and $C=2797.1 \pm 0.1$ Mc/sec, which lead to the structure as $d_{CI}=2.139 \pm 0.005$ Å and $\angle CCI=112^\circ 10' \pm 20'$ with the assumption of $d_{CC}=1.54$ Å. The calculation of the second order quadrupole effects for slightly asymmetric molecule with a plane of symmetry gave the asymmetry parameter $\eta=(q_{bb}-q_{cc})/q_{aa}$ of 0.205 ± 0.005 and $\xi=q_{ab}/q_{aa}$ of -0.57 ± 0.05 as well as the coupling constant eqQ of -1771 ± 10 Mc/sec along C-I bond. The components of the electric dipole moment were determined to be $\mu_a=1.75 \pm 0.05$ D and $\mu_b=0.25 \pm 0.1$ D. Centrifugal constants were obtained as $D_K=0.36 \pm 0.05$ Mc/sec, $D_{JK}=-0.151 \pm 0.005$ Mc/sec and $D_J < 0.05$ Mc/sec.

§ 1. Introduction

Microwave spectra of ethyl halide molecules have been reported by several authors¹⁾⁻⁵⁾, and the structure of ethyl fluoride, chloride, and bromide have been determined.

The molecule of ethyl iodide is a slightly asymmetric rotor with a very large quadrupole coupling constant. Various effects on the rotational levels, such as Stark effects, quadrupole effects, internal rotation effects can easily be treated by expansion in power series of the asymmetry parameter b .

The transitions which were convenient for the analysis of these effects were adopted. For example, the spectrum of hyperfine components corresponding to $F=9/2 \leftarrow 9/2$, $7/2 \leftarrow 7/2$, $9/2 \leftarrow 7/2$ and $7/2 \leftarrow 9/2$ of $J=3$, Q branch transition showed the separations only due to the

second order quadrupole effects. These lines were used to analyze the quadrupole effects. Stark shifts of $J_{K-1K_1}=1_{01} \leftarrow 0_{00}$ lines were used to determine the dipole moment for a reason of simplicity in calculation, and the lines with $K=1$ were found to reveal the abnormal hyperfine structure due to the hindered motion of methyl group.

The effects of internal rotation will be reported in the second part of this study.

§ 2. Experiments and Results

A typical Stark modulation spectrometer with 110 kc/sec sinusoidal wave modulation and phase sensitive detection was used. The ultimate sensitivity is estimated to be $\alpha_{\min} \approx 1 \times 10^{-8}$ cm⁻¹.

The wave guide absorption cells used were

Table I. Hyperfine structure of a-type transitions (frequencies in Mc/sec).

transition	observed frequency	$\Delta^{(1)}$	second order effects	calculated frequency	$\Delta^{(2)}$	ν_0
$1_{01} \leftarrow 0_{00}$						5775.83
7/2 $\leftarrow$ 5/2	5852.44	—	2.65	5852.48	0.08	
5/2 $\leftarrow$ 5/2	5542.08	—	2.92	5541.95	-0.13	
3/2 $\leftarrow$ 5/2	5988.1 $\pm$ 0.5	2.6	3.28	5987.5	-0.6	
$3_{21} \leftarrow 2_{20}$						17334.89
11/2 $\leftarrow$ 9/2	17443.60	-1.05	1.23	17442.65	-0.95	
9/2 $\leftarrow$ 7/2	17155.92	1.00	3.29	17157.11	1.11	
7/2 $\leftarrow$ 5/2	17227.84	—	0.75	17226.97	-0.87	
$3_{22} \leftarrow 2_{21}$						12330.19
11/2 $\leftarrow$ 9/2	17438.08	-2.11	1.22	17437.84	-0.24	
9/2 $\leftarrow$ 7/2	17152.32	-1.96	3.29	17152.55	0.23	
7/2 $\leftarrow$ 5/2	17227.84	—	0.78	17226.97	-0.87	
$3_{03} \leftarrow 2_{02}$						17323.88
11/2 $\leftarrow$ 9/2	17342.28	-0.63	-0.08	17341.56	-0.72	
9/2 $\leftarrow$ 7/2	17354.96	0.52	0.37	17355.85	0.89	
7/2 $\leftarrow$ 5/2	17283.82	2.45	2.15	17283.53	-0.29	
5/2 $\leftarrow$ 3/2	17212.40	-4.24	4.33	17212.46	0.06	
3/2 $\leftarrow$ 1/2	17194 $\pm$ 2	3	1.11	17192	-2	
9/2 $\leftarrow$ 9/2	17070.40	-0.74	-1.38	17069.99	-0.41	
3/2 $\leftarrow$ 3/2	17382.34	-1.13	3.18	17382.99	0.65	
$4_{31} \leftarrow 3_{30}, 4_{32} \leftarrow 3_{31}$						23107.00
13/2 $\leftarrow$ 11/2	23214.30	1.16	0.55	23214.02	0.27	
11/2 $\leftarrow$ 9/2	22968.75	-1.05	1.88	22968.78	0.03	
9/2 $\leftarrow$ 7/2	22978.44	0.47	0.66	22977.89	-0.55	
7/2 $\leftarrow$ 5/2	23116.56	-1.10	2.10	23116.31	-0.25	
$4_{22} \leftarrow 3_{21}$						23112.77
13/2 $\leftarrow$ 11/2	23167.05	-0.69	0.97	13167.41	0.36	
11/2 $\leftarrow$ 9/2	23059.77	1.96	-1.62	23060.11	0.34	
9/2 $\leftarrow$ 7/2	23050.34	-1.20	0.82	23049.95	-0.39	
7/2 $\leftarrow$ 5/2	23090.64	1.26	-0.29	23090.61	-0.03	
$4_{23} \leftarrow 3_{22}$						23105.14
13/2 $\leftarrow$ 11/2	23158.50	-0.48	1.03	23158.87	0.37	
11/2 $\leftarrow$ 9/2	23050.34	3.04	-2.53	23050.09	-0.25	
9/2 $\leftarrow$ 7/2	23042.24	-1.45	0.87	23041.43	-0.81	
7/2 $\leftarrow$ 5/2	23083.38	-1.14	-0.27	23082.88	-0.50	

an S band cell of four meters and an X band cell of three meters in length. The S band cell was used in the measurements of the frequencies corresponding to $J_{K-1, K-1} = 1_{01} \leftarrow 0_{00}$ transitions at 5.5 kMc/sec with a 2K26 klystron as the power source, and the X band cell was used for higher frequencies with the second or third harmonics from crystal multipliers driven by 2K26, X-12 and X-13 klystrons.

The ordinary commercial sample of ethyl iodide was used, and the wave guide cell was

cooled by dry ice to increase the intensity of the lines.

The frequency measurements were made with a frequency standard monitored against the 5 Mc/sec signal of JJY, and the accuracy of the measurements of frequencies are estimated to be ± 0.05 Mc/sec unless otherwise indicated.

The spectrum was observed in the frequency range from 5 to 30 kMc/sec. About fifty lines were found between 5.5 and 24 kMc/sec, and

Table II. Hyperfine structure of b-type transitions (frequencies in Mc/sec).

transition	observed frequency	$\Delta^{(1)}$	second order effects	calculated frequency	$\Delta^{(2)}$	ν_0
$2_{11} \leftarrow 2_{02}$						26507.00
$9/2 \leftarrow 9/2$	26438.02	-2.03	1.65	26439.22	1.20	
$7/2 \leftarrow 7/2$	26620 ± 2	-1	5.42	26618	-2	
$7/2 \leftarrow 5/2$	26538.5 ± 1	2	-0.23	26537.6	-1	
$5/2 \leftarrow 7/2$	26647.50	-4.65	5.15	26646.28	-1.22	
$3_{12} \leftarrow 3_{03}$						26784.14
$11/2 \leftarrow 11/2$	26745.74	-2.32	5.61	26745.75	0.01	
$9/2 \leftarrow 9/2$	26840.46	-4.16	3.88	26840.65	0.19	
$7/2 \leftarrow 7/2$	26835.20	4.58	-1.49	26835.25	0.05	
$7/2 \leftarrow 9/2$	26843.04	-5.91	6.07	26842.86	-0.18	
$5/2 \leftarrow 7/2$	26900 ± 1	1	3.13	26901	1	
$3/2 \leftarrow 5/2$	26928 ± 1	1	2.83	26928	1	
$4_{13} \leftarrow 4_{04}$						27156.96
$13/2 \leftarrow 13/2$	27110.00	17.02	-12.19	27109.76	-0.24	
$11/2 \leftarrow 11/2$	27196.26	-2.11	5.99	27196.34	0.08	
$9/2 \leftarrow 9/2$	27194.28	2.35	-4.23	27194.41	0.13	
$7/2 \leftarrow 7/2$	27161 ± 1	9.76	-9.60	27162	1	
$5/2 \leftarrow 5/2$	27126 ± 1	3.28	-4.17	27125	-1	
$3/2 \leftarrow 3/2$	27092.56	-6.54	5.14	27093.03	0.47	
$5_{14} \leftarrow 5_{05}$						27627.90
$15/2 \leftarrow 15/2$	27597.48	-3.32	-0.82	27597.41	-0.07	
$13/2 \leftarrow 13/2$	27639.18	8.09	-12.41	27639.22	0.03	
$11/2 \leftarrow 11/2$	27664.54	-7.14	-3.71	27664.05	-0.49	
$7/2 \leftarrow 7/2$	27596.0 ± 1	5.26	-16.46	27596.0	0.0	

Here, $\Delta^{(1)}$ and $\Delta^{(2)}$ indicate the discrepancies between the observed and the calculated frequencies, carried out with and without the second order quadrupole effects, respectively.

Frequency ν_0 is the resulting center frequency of hyperfine structure of the hypothetical rigid molecule.

other twenty, between 25 and 28 kMc/sec. The former lines were assigned to the R^a type transitions ($\Delta K_{-1}=0$, $\Delta J=1$) corresponding to $J=1 \leftarrow 0$, $3 \leftarrow 2$ and $4 \leftarrow 3$, and the latter to the Q^b type transitions ($\Delta K_{-1}=1$, $\Delta J=0$) corresponding to $J=2$, 3, 4 and 5. The observed frequencies are listed in the second column of Tables I and II. The lines which show abnormal hyperfine structure due to the hindered motion are excluded from these tables⁶.

§ 3. Theoretical Consideration

(a) Quadrupole interaction

The first order quadrupole energy can be written

$$W_Q = \frac{2J+3}{J} f(I, J, F) \cdot e q_J Q \quad (1)$$

where $f(I, J, F)$ is the Casimir's function, q_J

the field gradient along the space fixed Z -direction averaged by the rotational wave function, and Q the nuclear quadrupole moment⁷. The field gradient q_J is expanded in power series of the asymmetry parameter b . It is conveniently written

$$q_J = \frac{q_m}{(J+1)(2J+3)} \{3K^2 - J(J+1) - 3C_2 b^2 - \eta(C_1 + 2C_2 b^2 + 3C_3 b^3)\} + \dots \quad (2)^*$$

where C_n is the coefficient of b^n in the expansion of rotational energies, and $\eta = (q_{xx} - q_{yy})/q_{zz}$ the asymmetry parameter of quadrupole coupling constant.

To calculate the second order terms of the

* This expression was first given by G. K. Kight and B. T. Felt and have been corrected by J. K. Kraitchman and A. Javan, and here η is taken as $(q_{bb} - q_{cc})/q_{aa}$.

quadrupole interaction energy, the basic form of Hamiltonian must be used, which is written in the form of inner product, $H_Q = -\frac{1}{6} \mathbf{Q} : \nabla \mathbf{E}$, between the quadrupole moment dyadic $\mathbf{Q}$, and the gradient of the electric field about the nucleus $\nabla \mathbf{E}^{(7)}$. The only matrix elements $\langle IFJ\tau | H_Q | IFJ'\tau' J \rangle$ which appear in this order of perturbation are those for which $J' = J, J \pm 1$ and $J \pm 2$. When a numerical factor evaluated by Bragg⁸⁾ is separated again, they are reduced to the matrix elements of ZZ component of $\nabla \mathbf{E}$, which is further expanded in terms of components along the molecular fixed axis x, y, z ,

$$\nabla E_{ZZ} = \sum_{\mu} \alpha_{Z\mu}^2 q_{\mu\mu} + \sum_{\mu, \nu} \alpha_{Z\mu} \alpha_{Z\nu} q_{\mu\nu}, \quad \mu, \nu = (x, y, z) \quad (3)$$

where $\alpha_{Z\mu}$ is the direction cosine between Z and μ axis.

The first summation of Eq. (3) belongs to the representation A of Four group, and is written in the form

$$\left\{ \frac{1}{2}(3\alpha_{ZZ}^2 - 1) + \frac{1}{4}(\alpha_{+}^2 - \alpha_{-}^2)\eta \right\} q_m, \quad \alpha_{\pm} = \alpha_{Z\pm} \pm i\alpha_{Zy}, \quad (4)$$

by using the relations $\sum_{\mu} \alpha_{Z\mu}^2 = 1$ and $\sum_{\mu} q_{\mu\mu} = 0$. If the slightly asymmetric molecule is assumed to have a plane of symmetry, the second summation of Eq. (3) is identically zero except one term. The remaining term is written in the form

$$\alpha_{Z\mu} \alpha_{Z\nu} \xi q_{z\mu}$$

with the parameter $\xi = q_{\mu\nu}/q_{zz}$, and belongs to the representation B_x or B_y according to whether (μ, ν) is (y, z) or (z, x) .

The only non vanishing matrix elements belong to representation A , and the connecting states are restricted to the cases shown in Table III, from which ΔK_{-1} or ΔK_1 and ΔJ are determined.

Table III. Connection of energy levels through the terms of species A, B_x and B_y .

ΔJ	even	odd
Species		
A	$E^{\pm} \longrightarrow E^{\pm}$	$E^{\pm} \longrightarrow E^{\mp}$
	$O^{\pm} \longrightarrow O^{\pm}$	$O^{\pm} \longrightarrow O^{\mp}$
B_x	$E^{\pm} \longrightarrow O^{\mp}$	$E^{\pm} \longrightarrow O^{\pm}$
B_y	$E^{\pm} \longrightarrow O^{\pm}$	$E^{\pm} \longrightarrow O^{\mp}$

Here E, O and $\pm$ indicates the evenness or oddness of K and γ , respectively⁹⁾.

The wave function of a slightly asymmetric rotor is expanded in terms of the Wang's symmetric limit wave function $S_{JK\gamma}^{(10)}$

$$\psi_{JK\gamma} = S_{JK\gamma} + \alpha(JK\gamma)S_{JK-2\gamma} + \beta(JK\gamma)S_{JK+2\gamma} + \dots \quad (5)$$

where the coefficients α, β have been obtained by Lide^{11)*}. When the terms higher than δ^2 are neglected the matrix elements, $\langle JK\gamma J | \nabla E_{ZZ} | J'K'\gamma' J \rangle$, for which $J' = J, J \pm 1, J \pm 2, K' = K, K \pm 1, K \pm 2$ and γ' as indicated above, are obtained to the order of δ . The squares of these elements are divided by the difference of rotational energy $W_{JK\gamma}$, and summed up for J and K , to give the second order interactions;

$$W^{(2)}(IFJK) = \sum_{J'} g_{J'}^2 (IFJ) \sum_{K'\gamma'} \frac{|(JK\gamma J | \nabla E_{ZZ} | J'K'\gamma' J)|^2}{W_{JK\gamma} - W_{J'K'\gamma'}} (eQ)^2. \quad (6)$$

Here, g_J is the numerical factor given by Bragg⁸⁾.

If it is assumed that the q -tensor is cylindrically symmetric along the bond in question, and that the principal axis of the tensor is strictly on the bond axis, η and ξ are written in terms of an angle ϕ between the bond and the principal axis of inertia;

$$\eta = \frac{3 \sin^2 \phi}{3 \cos^2 \phi - 1}, \quad (7-a)$$

$$\xi = -\frac{3 \sin \phi \cos \phi}{3 \cos^2 \phi - 1}. \quad (7-b)$$

However, η and ξ can be derived from the analysis of the first and second order quadrupole effects, respectively. If the second order energy is separated from the first order one, the analysis of the major part of hyperfine energy can be easily carried out to give the very accurate value on η . For this purpose a set of hyperfine components is adopted for which the first order quadrupole effects have the same contribution, and the separations of the spectral lines come from the effects of higher order of quadrupole energy. Eq. (1) gives the first order energy, where $f(JF)$ is the Casimir's function;

* According to the table given by Lide, $\beta(J1\gamma)$ and $\alpha(J3\gamma)$ are given by $\pm(1/16)f(J, 2)^{1/2}[\delta + (-1)^{\gamma} \times J(J+1)\delta^2/32]$, respectively, but the sign before $J(J+1)$ should be reversed.

$$\left. \begin{aligned} f(IJF) &= \frac{3C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)} \\ \text{and} \\ C &= F(F+1) - I(I+1) - J(J+1) \end{aligned} \right\} \quad (8)$$

Since the following equation

$$f(IJF) = f(IJF+1)$$

is satisfied only when $I=5/2$, $J=3$ and $F=7/2^*$, the hyperfine components corresponding to $F=9/2 \leftarrow 9/2$, $7/2 \leftarrow 7/2$, $9/2 \leftarrow 7/2$ and $7/2 \leftarrow 9/2$ of $J=3$ Q branch lines show the same amount of shifts due to the first order quadrupole interaction.

Thus the first and second order energy can be treated separately for these spectral lines, and the initial values of η and ξ estimated by Eq. (7) are improved to a considerable extent. First, crude values of η and $(eqQ)_{aa}$ are estimated from the analysis of the first order shifts of these lines, and the remaining discrepancies for each spectrum are attributed to the second order quadrupole effects. From these discrepancies, more accurate value of ξ is determined. Then the second order quadrupole shifts are subtracted from these spectrum to improve the values of η and $(eqQ)_{aa}$. The above procedure is repeated until the molecular constants η , ξ and $(eqQ)_{aa}$ converge to constant values.

The values of η and ξ thus obtained are used to evaluate each component of q -tensor, the diagonalization of which leads to the determination of angle ϕ' , between the principal axis of q -tensor and that of moment of inertia. It should be compared to ϕ in Eq. (7), geometrically obtained from the structure.

(b) Stark energy

Stark effects in an asymmetric rotor molecule with the quadrupole coupling in the "intermediate field" case can be obtained by solving the secular equation derived from the Hamiltonian, $H = H_0 + H_Q + H_E$, where H_0 is the unperturbed rotational energy, and H_E is the perturbation due to the electric field. When the electric field is strong, the J, m_J representation is appropriately used as was proposed by Mizushima¹²⁾. In the case of ethyl iodide, on the contrary, the F, M_F , re-

presentation is more convenient owing to the large quadrupole coupling energy. This method was developed by Low and Townes for the case of symmetric top molecules¹³⁾. But some modification is necessary for the asymmetric rotor on account of the second order feature of Stark energy.

To evaluate the Stark coefficient of a certain rotational level, the secular equation is set up for the considered J and τ . The Stark energy, H_E , however, has no terms in the submatrices of $J\tau$, in F, M_F representation**, while the quadrupole energy, H_Q , has the diagonal elements with respect to F, M_F (Eq. (1)). The only non vanishing matrix elements of H_E are those which connect the different $J\tau$, according to the selection rules for the transitions, and H_Q has also $J\tau \leftrightarrow J'\tau'$ interaction through the part of the field gradient. Since the rotational energies of such states differ considerably from each other, the above contribution can be handled by the perturbation theory developed by Van Vleck¹⁶⁾, which modifies the secular determinant of considering $J\tau$ by an additional Hamiltonian of the form¹⁶⁾;

$$H_{ij} - \frac{1}{2} \sum_m \left(\frac{H'_{im} H'_{jm}}{W_i - W_m} + \frac{H'_{im} H'_{jm}}{W_j - W_m} \right) \quad (12)$$

where H' is

$$\left. \begin{aligned} &H_Q + H_E \\ \text{and} \\ &H'_{im} = \sum_{m_J} C^*(IFM_F J\tau m_J) C(IF' M_F J'\tau' m_J) \\ &\quad \times \langle J\tau m_J | H' | J'\tau' m_J \rangle, \end{aligned} \right\} \quad (13)$$

** The base function, $\Psi(IFM_F J\tau)$, is constructed from the rotational wave function of the asymmetric rotor, $\phi(J\tau m_J)$, and the nuclear spin function, $\phi(I m_I)$, using the Wigner's coefficient, $C(IFM_F J\tau m_J)$,¹⁴⁾

$$\Psi(IFM_F J\tau) = \sum_{m_J} C(IFM_F J\tau m_J) \phi(J\tau m_J) \phi(I m_I). \quad (10)$$

The Stark energy $H_E = \mu \cdot E$, where μ is the electric dipole moment, is diagonal with respect to M_F . And the matrix elements between the states of same J, τ and M_F are reduced to the form;

$$\begin{aligned} &\langle IFM_F J\tau | H_E | IF' M_F J\tau \rangle \\ &= \sum_{m_J} C^*(IFM_F J\tau m_J) C(IF' M_F J\tau m_J) \langle H_E \rangle. \end{aligned} \quad (11)$$

Here $\langle \rangle$ is the average over $J\tau m_J$ states, and is identically zero from the symmetry, because no term in $\mu \cdot E$ belongs to the representation A .

* C must take the value n and $-(n+1)$ corresponding to $F+1$ and F , and the following condition must be satisfied, $2F+4F+3-2I(I+1)-2J(J+1)=0$. (9)

and $\sum_m$ stands for summation over J , τ and F . Using the expansion of the asymmetric rotor wave function $\phi(J\tau m_J)$ in the way of Eq. (5), we can evaluate the last elements of Eq. (13) in terms of δ . The elements of H_Q in H' are calculated by the method as described in (a), and those of H_B are given by Lide¹⁰.

In the interactions of Eq. (12), M_F still remains constant, and the Stark coefficients of R branch transition, for instance, can be determined by solving the secular equation for the lowest value of M_F . It is $(2I+1)$ -th or $(2J+1)$ -th degree and each eigenvalue gives the Stark coefficient of hyperfine component corresponding to $F=I+J, \dots |I-J|$.

§ 4. Discussion

The frequencies of the quadrupole hyperfine structure calculated by the first order treatment alone could not satisfactorily be fitted to the observed spectrum. The discrepancies between the calculated and the observed frequencies are listed in the column of $\Delta^{(1)}$ in Tables I and II. The second order effects evaluated to the first order of asymmetry parameter and the calculated frequencies are listed in Tables I and II, together with the discrepancies for this case. The last column of these tables show the central frequencies of the hyperfine structure.

The centrifugal distortion effect was considered in the analysis of the rotational energies. The approximate expression for R^a type transition is

$$\Delta\nu = -4D_J(J+1)^3 - 2D_{JK}(J+1)K^2, \quad (14)$$

and for Q^b type transition is

$$\Delta\nu = -4D_{JK}J(J+1) - D_K. \quad (15)$$

Table IV lists the rotational constants and the centrifugal constants used in the analysis.

Table IV. Rotational constants and centrifugal constants in Mc/sec.

A	29119.9 $\pm$ 0.1	D_K	0.36 $\pm$ 0.05
B	2979.2 $\pm$ 0.1	D_{JK}	-0.151 $\pm$ 0.005
C	2797.1 $\pm$ 0.1	D_J	<0.5

If the torsional motion of the methyl group is taken into account the effective rotational constant A , for the Q^b type transitions corresponding to the A state of the hindered motion is expressed as¹⁷,

$$A = \frac{h}{8\pi^2 I_z} + Q(1+4F\rho)_A/F. \quad (16)$$

Here

$$F = hI_x I_z / 8\pi^2 d I_\alpha, \quad Q = hI_x \lambda_z / 8\pi^2 d, \\ d = I_x(I_x - I_\alpha \lambda_z^2) - I_\alpha \lambda_z^2 I_z,$$

in which I_α is the moment of inertia of methyl group about its symmetry axis, λ_x and λ_z the direction cosines of this axis, and

Table V. Structural constants of ethyl halides.

structural parameters	C_2H_5I	$C_2H_5Br^{(3)}$	$C_2H_5Cl^{(2)}$	$C_2H_5Cl^{(4)}$	$C_2H_5F^{(1)}$
d_{CX}	2.139 $\pm$ 0.005 Å	1.9400 $\pm$ 0.0004 Å	1.7785 $\pm$ 0.0003 Å	1.78 Å	1.375 Å
d_{CC}	1.540 Å (ass.)	1.5495 $\pm$ 0.0005 Å	1.5495 $\pm$ 0.0005 Å	1.54 Å	1.540 Å
$\angle CCX$	112°10' $\pm$ 20'	110°30' $\pm$ 2'	110°30' $\pm$ 2'	110°30'	109°28'
d_{CH}	1.11 Å (ass.)	1.11	1.101 $\pm$ 0.003 Å		1.091 Å
$\angle HCH$	110°00' (ass.)	110°00'	110°00' $\pm$ 30'		109°28'

$$\rho = |p_{vv'}|^2 / (E_v - E_{v'}),$$

E_v the eigenvalue of Mathieu function, p the angular momentum of methyl group. The factor $(1+4F\rho)_A$ is given in terms of the barrier height V_3 or parameter $S=4V_3/9F$, by the semiempirical relation proposed by Swalen¹⁸. The barrier height of about $V_3=2.4$ kcal/mole for ethyl iodide evaluated from the abnormal hyperfine structure in the $K=1$ lines of R^a type transition⁶ enables one to estimate the correction in Eq. (16).

The corrected rotational constants (shown in Table VI.) gave the structural constants of ethyl iodide, and they are compared to those of other ethyl halides in Table V.

The model described above reproduces the rotational constants as shown in Table VI. The angle ϕ between the principal axis of inertia and the C-I bond was obtained to be $\phi=19^\circ \pm 30'$.

Two values of η and ξ , estimated by Eq. (7) and determined by experiments by the method

Table VI. Rotational constants.

	exp. (corrected)	calc.	Δ (in Mc/sec.)
A	29106.2	29133.03	26.8
B	2979.2	2976.75	-2.4
C	2797.1	2799.20	7.1
b_D		-0.003474	

Table VII. Constants of quadrupole coupling.

	calc.	exp.
η	0.20 ± 0.01	0.205 ± 0.005
ξ	-0.56 ± 0.01	-0.57 ± 0.05
$(eqQ)_{aa}$		-1481.9 ± 0.5 (Mc/sec)

described above, are listed in Table VII, with the quadrupole coupling constant $(eqQ)_{aa}$.

From this results, all the components of eqQ -tensor is obtained with the assumption of having a plane of symmetry,

$$eqQ \begin{bmatrix} q_{aa} & 0 & 0 \\ 0 & q_{bb} & q_{ab} \\ 0 & q_{ab} & q_{aa} \end{bmatrix} = \begin{bmatrix} 893 \pm 10 & 0 & 0 \\ 0 & 584 \pm 10 & 884 \pm 50 \\ 0 & 884 \pm 50 & -1481.9 \pm 0.5 \end{bmatrix} = T^{-1} \begin{bmatrix} 893 \pm 10 & 0 & 0 \\ 0 & 878 \pm 50 & 0 \\ 0 & 0 & -1771 \pm 10 \end{bmatrix} T.$$

Here T is the rotational operation in the plane of symmetry, the angle of which, ϕ' was given by $\phi' = 20^\circ 10' \pm 1^\circ$.

The discrepancies between ϕ and ϕ' is about one degree. It may be said that the principal axis of q -tensor is parallel to the bond axis within the experimental accuracy.

Table VIII. Quadrupole coupling constants along the C-I bond.

C_2H_5I	-1771 (Mc/sec)
$C_2H_5I^{(19)}$	-1788
$CH_3I^{(20)}$	-1934
$CF_3I^{(21)}$	-2143.8
$CH_3CCI^{(22)}$	-2230
$ICN^{(23)}$	-2420

The value of eqQ of -1771 ± 10 Mc/sec along the bond is compared to those of other iodides in Table VIII.

According to the equation derived by Townes and Dailey⁽²⁴⁾, the ionic character of C-I bond was estimated to be 9%.

The electric dipole moment was determined

from the Stark shifts of hyperfine components corresponding to $F=7/2 \leftarrow 5/2$ and $5/2 \leftarrow 3/2$ of $J_{K-1K_1}=1_{01} \leftarrow 0_{00}$ transition. The secular equation of the third order constructed for $M_F = \frac{1}{2}$ was solved, and the component of the dipole moment parallel to the z axis was given as $\mu_{||} = 1.75 \pm 0.05$ D, and the perpendicular component, $\mu_{\perp} = 0.25 \pm 0.1$ D. The value of $|\mu| = 1.77 \pm 0.1$ D was in agreement with the former result $\mu = 1.87$ D obtained from the measurements of dielectric constants⁽²⁵⁾. The obtained values of $\mu_{||}$ and $\mu_{\perp}$ determined the direction of dipole moment as shown in Fig. 1. A small deviation from C-I bond comes from the polarization of C-C bond.

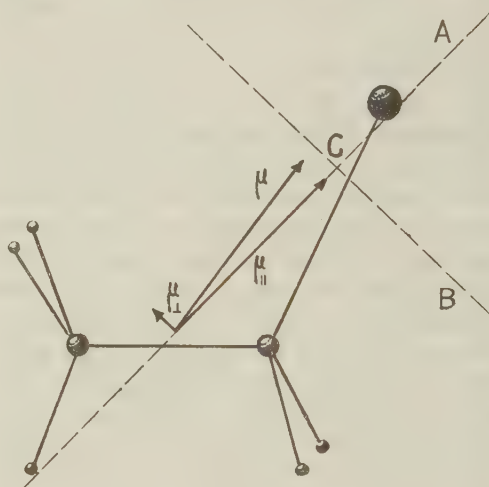


Fig. 1. Dipole moment of ethyl iodide.

The barrier height of about 2.4 kcal/mole is not accurate enough to be compared with those of C_2H_5Br and C_2H_5Cl recently reported by Lide⁽⁹⁾. The more precise analysis of the internal rotation phenomena is now in progress and will be reported later.

Acknowledgement

The authors wish to express their gratitude to Professor Koichi Shimoda for his kind guidance and encouragement throughout the course of this investigation. They are also indebted to Mr. Kunitaka Kondo for his assistance in some of the measurements, and to Dr. Eizi Hirota of Department of Chemistry for many clarifying discussions.

References

- 1) J. Kraitchman and B. P. Dailey: J. Chem. Phys. **23** (1955) 185.

- 2) R. S. Wagner and B. P. Dailey: J. Chem. Phys. **26** (1957) 1588.
- 3) R. S. Wagner, B. P. Dailey and N. Solimene: J. Chem. Phys. **26** (1957) 1593.
- 4) А. И. Барчуков, Т. М. Мурина, А. М. Прохоров: Оптика и спектроскопия, IV (1958) 521.
- 5) D. R. Lide, Jr.: J. Chem. Phys. **30** (1959) 37.
- 6) T. Kasuya and T. Oka: J. Phys. Soc. Japan **14** (1959) 980.
- 7) C. H. Townes and A. L. Schawlow: *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955).
- 8) J. K. Bragg and S. G. Golden: Phys. Rev. **75** (1948) 735.
- 9) P. C. Cross, R. M. Hainer and G. W. King: J. Chem. Phys. **12** (1948) 210.
- 10) S. C. Wang: Phys. Rev. **34** (1929) 243.
- 11) D. R. Lide, Jr.: J. Chem. Phys. **20** (1952) 1761.
- 12) M. Mizushima: J. Chem. Phys. **21** (1953) 539.
- 13) W. Low and C. H. Townes: Phys. Rev. **76** (1949) 1295.
- 14) E. U. Condon and G. H. Shortley: *The Theory of Atomic Spectra* (Macmillan Co., New York, 1935) 76.
- 15) E. C. Kemble: *Fundamental Principle of Quantum Mechanics* (McGraw-Hill Book Co., New York, 1937) 395.
- 16) S. Golden and E. B. Wilson, Jr.: J. Chem. Phys. **16** (1948) 669.
- 17) R. W. Kilb, C. C. Lin and E. B. Wilson, Jr.: J. Chem. Phys. **26** (1957) 1695.
- 18) J. D. Swalen: J. Chem. Phys. **23** (1955) 1739.
- 19) H. W. Morgan and J. H. Goldstein: J. Chem. Phys. **22** (1954) 1427.
- 20) W. Gordy, J. S. Simmons and A. W. Smith: Phys. Rev. **74** (1948) 243.
- 21) F. Sterzer: J. Chem. Phys. **22** (1954) 2094.
- 22) J. Sheridan and W. Gordy: J. Chem. Phys. **20** (1952) 735.
- 23) C. H. Townes, A. N. Holden and F. R. Merritt: Phys. Rev. **74** (1948) 1113.
- 24) C. H. Townes and B. P. Dailey: J. Chem. Phys. **23** (1955) 118.
- 25) L. G. Groves and S. Sugden: J. Chem. Soc. (1937) 158.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 2, FEBRUARY, 1960

Microwave Zeeman Effect of Formaldehyde

Kunitaka KONDO, Hiromasa HIRAKAWA*, Akira MIYAHARA**,
Takeshi OKA and Koichi SHIMODA

Department of Physics, Faculty of Science, University of Tokyo, Tokyo

(Received October 3, 1959)

Zeeman effects in the absorption spectra of formaldehyde H_2CO , HDCO , and D_2CO were studied in microwave region with magnetic field of 1500~300 oersteds. The effective g -values in several rotational states and the elements of g -tensor g_{aa} , g_{bb} , and g_{cc} of these molecules were determined.

Dependences of the effective g -values on the rotational quantum numbers J, τ were consistent among these isotopically substituted molecules. The components of the g -tensors of these molecules have been found to be $g_{aa}=2.86\pm0.04$ for H_2CO , 2.00 ± 0.05 for HDCO , and 1.46 ± 0.05 for D_2CO . They are extraordinarily large compared to those of other molecules already known. A brief qualitative interpretation is given.

§ 1. Introduction

The electronic ground states of formaldehyde H_2CO , HDCO , and D_2CO are $^1\Sigma$. These

* Present Address: Japan Atomic Energy Research Institute, Ibaragi, Japan.

** Present Address: Institute for Nuclear Study, University of Tokyo, Tanashi-machi, Tokyo Japan.

molecules have rotational magnetic moments of the order of nuclear magnetons due to the end-over end rotation. The magnetic hyperfine structures observed by the molecular beam maser experiment¹⁾ are small, so that it is reasonable to neglect the hyperfine structures in considering the Zeeman effect.

Theories of Zeeman effects of such $^1\Sigma$ -molecules have been given by several authors²⁾⁵⁾. The Zeeman energy of a molecule in a external magnetic field H is

$$W = -\mu_n g_J M H, \quad (1)$$

where μ_n is the nuclear magneton, M the magnetic quantum number of the rotational angular momentum J , and g_J the effective g -factor in a given rotational state. The g -factor g_J is expressed as⁶⁾

$$g_J = \frac{1}{2} \left\{ 1 + \frac{1}{J(J+1)} \left[E(\kappa) - (\kappa+1) \frac{dE(\kappa)}{d\kappa} \right] \right\} g_{aa} + \frac{1}{J(J+1)} \frac{dE(\kappa)}{d\kappa} g_{bb} + \frac{1}{2} \left\{ 1 - \frac{1}{J(J+1)} \left[E(\kappa) - (\kappa-1) \frac{dE(\kappa)}{d\kappa} \right] \right\} g_{cc}, \quad (2)$$

where κ is Ray's asymmetry parameter and $E(\kappa)$ is defined by the formula of the energy of an asymmetric rotor

$$W = \frac{1}{2} (A+C)J(J+1) + \frac{1}{2} (A-C)E(\kappa). \quad (3)$$

The element of the g -tensor $g_{\mu\nu}(\mu, \nu=a, b, c)$ is given by a formula⁴⁾,

$$g_{\mu\nu} = \frac{M_p}{I_\nu} \left[\sum_K Z_K (|X_K|^2 \delta_{\mu\nu} - X_{K\mu} X_{K\nu}) - \frac{1}{m} \sum_n' \frac{\langle 0 | L_\mu | n \rangle \langle n | L_\nu | 0 \rangle + \langle 0 | L_\nu | n \rangle \langle n | L_\mu | 0 \rangle}{E_n - E_0} \right], \quad (4)$$

where I_ν is the moment of inertia around a -axis and M_p is the mass of proton. The first term of the right hand side of Eq. (4) is the nuclear contribution to the magnetic moment and the summation is to be taken over all nuclei, where $X(X_{Ka}, X_{Kb}, X_{Kc})$ is the position of K -th nucleus with electronic charge Z_{Ke} . The second term is the electronic contribution due to the partial excitation of electronic state by the rotation of molecule and the summation is to be taken over every possible electronic excited state where L_μ , or L_ν is the electronic angular momentum around μ - or ν -axis. The observed lines are those of electric dipole transitions between K -type doubling levels and the microwave electric field is perpendicular to the dc magnetic field in the present experimental apparatus.

The selection rules in this case are

$$\Delta J = 0, \quad \Delta M = \pm 1, \quad \Delta K_{-1} = 0, \quad (5)$$

and the transition frequencies are

$$\nu = \nu_0 - \frac{\mu_n M}{h} (g_1 - g_2) M \mp \frac{\mu_n}{h} g_1 H, \quad (6)$$

where ν_0 is the frequency for the pure rotational transition and g_1 and g_2 are the g -values of upper and lower levels, respectively.

The g -factor of an asymmetric molecule can be expressed by a g -tensor with nonvanish-

ing off-diagonal elements $g_{\mu\nu}(\mu \neq \nu)$. However, such a molecule with C_{2v} symmetry as H_2CO and D_2CO has a diagonal g -tensor.

§ 2. Experiment and Analysis

A 5000 Mc wave guide (2.5 cm $\times$ 5 cm) absorption cell of 100 kc Stark modulation type was inserted in a solenoidal coil of 35 cm length and of 7 cm inner diameter. The magnetic field strength was 165 ± 3 oersteds/ampere, and the current of 10~20 A was applied. The magnetic field was measured by an electronic fluxmeter. The sinusoidal Stark-modulation with dc bias electric field was used to observe the lines. To obtain the Zeeman pattern of the spectral lines the observed frequencies were extrapolated to those for zero electric field⁹⁾. Each line was observed to split into two components in a magnetic field, and no further splittings of each component nor broadening of the lines, as is expected from the second terms on the right hand side of Eq. (4), were observed. Thus the difference of the g -values for the upper and lower levels could not be found, that is, $g_1 - g_2 \approx 0$. The central frequency of the two components are calculated as $\nu_0 \pm ((g_1 + g_2)/2h)\mu_n H$ considering the frequencies and relative intensities of all transitions between various M -states. Effective g -values

Table I. *g*-factors in various transitions of formaldehyde.

Molecules	Transitions	Frequencies (Mc)	Effective <i>g</i> -values in terms of g_{aa} , g_{bb} , g_{cc} of H_2CO (calc)	Effective <i>g</i> -factors (obs)	Effective <i>g</i> -factors (calc)
H_2CO	$1_{1,1} \rightarrow 1_{1,0}$	4829.73	$0.5000g_{aa} + 0.2500g_{bb} + 0.2500g_{cc}$	1.50 ± 0.02	1.53
	$2_{1,2} \rightarrow 2_{1,1}$	14488.65	$0.1667g_{aa} + 0.4167g_{bb} + 0.4167g_{cc}$	0.615 ± 0.02	0.622
$HDCO$	$1_{1,1} \rightarrow 1_{1,0}$	5346.64	$0.3495g_{aa} + 0.2473g_{bb} + 0.2208g_{cc}$	1.13 ± 0.01	1.10
	$2_{1,2} \rightarrow 2_{1,1}$	16038.06	$0.1164g_{aa} + 0.3835g_{bb} + 0.3680g_{cc}$	0.49 ± 0.01	0.47
	$5_{2,4} \rightarrow 5_{2,3}$	4489.08	$0.0934g_{aa} + 0.4186g_{bb} + 0.3621g_{cc}$	0.38 ± 0.01	0.41
D_2CO	$1_{1,1} \rightarrow 1_{1,0}$	6096.10	$0.2516g_{aa} + 0.2100g_{bb} + 0.1950g_{cc}$	0.83 ± 0.02	0.80
	$2_{1,2} \rightarrow 2_{1,1}$	18287.90	$0.0839g_{aa} + 0.3500g_{bb} + 0.3250g_{cc}$	0.36 ± 0.02	0.36
	$4_{2,3} \rightarrow 4_{2,2}$	3682.28	$0.1003g_{aa} + 0.3100g_{bb} + 0.2914g_{cc}$	0.39 ± 0.01	0.39

in terms of the elements of *g*-tensor were obtained by the Eq. (2) using the rotational constants of these molecules obtained in this laboratory⁷). The effective *g*-values of isotopically substituted molecules are expressed in terms of a *g*-tensor of any one molecule, because it is plausible to assume same electronic structures for the isotopically substituted molecules. In Table I *g*-values expressed in terms of g_{aa} , g_{bb} , and g_{cc} of H_2CO are listed.

Table II. *g*-values of formaldehydes.

Molecules	$ g_{aa} $	$ g_{bb} $	$ g_{cc} $
H_2CO	2.90 ± 0.05	0.35 ± 0.10	0.02 ± 0.10
$HDCO$	2.00 ± 0.05	0.32 ± 0.10	0.02 ± 0.10
D_2CO	1.46 ± 0.05	0.29 ± 0.10	0.02 ± 0.10

The present experiment gives only absolute values of the effective *g*-tensors, which are shown in the next to the last column in Table I. If it is assumed, however, that all the observed effective *g*-factors have the same signs, the elements of *g*-tensor, g_{aa} etc, can be determined by the following procedure.

First solving six equations in Table I by the method of least mean square with the above assumptions, the absolute values of

$g_{\mu\nu}$'s are calculated as in Table II, where the g_{aa} and g_{bb} are found to have the same signs, and the magnitude of g_{cc} is quite small. It can be shown from Eq. (4) that $g_{\mu\nu}$ can not be larger than +1, and if $|g_{\mu\nu}| > 1$, $g_{\mu\nu}$ must be negative. This may be the case if the magnitude of the electronic term in Eq. (4) is sufficiently large. Therefore the signs of g_{aa} and g_{bb} are concluded to be negative.

The effective *g*-factors calculated from the equations in Table I and the values of g_{aa} , g_{bb} , and g_{cc} in Table II are in close agreement with the experimental results as shown in the last column of Table I.

§ 3. Discussions

With the aid of Eq. (4), the diagonal elements of *g*-tensor can be expressed as

$$\frac{I_a}{2M_p} g_{aa} = \sum_K \frac{Z_K}{2} (b_K^2 + c_K^2) - \frac{1}{m} \sum_n' \frac{|\langle 0 | L_a | n \rangle|^2}{E_n - E_0} \quad (7)$$

with similar expressions for g_{aa} and g_{cc} . The left hand side of Eq. (7) and the first term on the right hand side can be calculated from the molecular constants and *g*-values in Table II. The calculated electronic contributions are shown in Table III. If the inner shell

Table III. The nuclear and electronic contributions to the magnetic moment of H_2CO .

	nuclei	electrons	total
	$\sum_K \frac{Z_K}{2} (X_K ^2 \delta_{\mu\nu} - X_K \mu^2)$	$-\frac{1}{m} \sum_n' \frac{ \langle 0 L_\mu n \rangle ^2}{E_n - E_0}$	$\frac{I_\mu}{2M_p} g_{\mu\mu}$
<i>a</i> -axis	$0.92 \text{ \AA}^2$	$-3.47 \text{ \AA}^2$	$-2.56 \text{ \AA}^2$
<i>b</i> -axis	3.9	-0.1	-2.2
<i>c</i> axis	4.8	-5.1	+0.3

electrons are assumed to be fixed to the nuclei and valence electrons to the middle of the bonds, the second term in Eq. (7) is transformed into

$$-\frac{1}{2}\sum_i(x_{ib}^2+x_{ic}^2)$$

where x_{ib} and x_{ic} are coordinates of the i -th electron.

Although such a "frozen" charge approximation does not give correct values of

Table IV. Molecular g Factors for Hydride Molecules in $^1\Sigma$ States.

Molecule	g (observed)	g (calculated by a frozen charge approximation)
H ₂	$+0.8829\pm0.00007^a$	+1.00
NH ₃	$g_{zz}=0.484\pm0.0007^{b,c}$	+0.50
	$g_{xx}=g_{yy}=0.560\pm0.007^c$	+0.60
H ₂ O	$g_{aa}=0.585^{b,d}$	+0.60
	$g_{bb}=0.742^{b,d}$	+0.50
	$g_{cc}=0.666$	+0.51
H ₂ S	$g_{aa}=\pm0.355\pm0.008^e$	+0.56
	$g_{bb}=\pm0.195\pm0.008^e$	+0.50
	$g_{cc}=\pm0.209\pm0.008^e$	+0.53
CH ₃ CCH	$g_{zz}=0.298^f$	+0.50
	$g_{xx}\simeq0$	+0.09
CH ₃ F	$g_{zz}=0.487$ or 0.612^g	+0.50
	$g_{xx}=\pm0.0624^g$	+0.07
H ₂ CO	$g_{aa}=-2.90\pm0.05$	+0.50
	$g_{bb}=-0.35\pm0.10$	+0.08
	$g_{cc}=0.02\pm0.10$	+0.13

- a. N. J. Harrick and N. F. Ramsay: Phys. Rev. **88** (1952) 228.
- b. C. K. Jen: Phys. Rev. **81** (1951) 197.
- c. J. R. Eshbach and M. W. P. Strandberg: Phys. Rev. **82** (1951) 327 A.
- d. R. F. Schwarz: Phys. Rev. **86** (1952) 606 A.
- e. C. A. Burrus: J. Chem. Phys. **30** (1959) 976.
- f. J. T. Cox, P. B. Peyton, Jr. and W. Gordy: Phys. Rev. **92** (1953) 274.
- g. J. T. Cox and W. Gordy: Phys. Rev. **101** (1956) 1298.

g -factors, it is interesting to see that this assumption can explain qualitatively the observed g -factors of almost all hydride molecules. This assumption, however, fails in the estimation of g -value in the case of formaldehyde, as is shown in the Table IV⁸⁾. It will be due to the neglect of the contribution of two electrons bonding carbon and oxygen atoms, and a lone pair of electrons around the oxygen atom, whose positions are considered to be protruding out of the molecular axis. They give negative magnetic moments when the molecule rotates around a -axis. If the valence electrons bonding carbon and hydrogen atoms are assumed to be fixed at the middle of the bonds, the effective mean radius of these four electrons, a couple of π -electrons and a lone pair of electrons, is

$$r_{\text{eff}}=\frac{1}{2}\sqrt{\frac{I_a}{M_p}}\left|g_{aa}\right|+(b^2+c^2)=1.2\text{ A},$$

which seems to be a reasonable value.

§ 4. Acknowledgement

The authors are indebted to Dr. T. Nishikawa for his helpful discussions, and to Mr. T. Kasuya for his assistance in the measurements.

References

- 1) H. Takuma, T. Shimizu, and K. Shimoda: J. Phys. Soc. Japan **14** (1959) 1595.
- 2) G. C. Wick: Z. Phys. **85** (1933) 25; Phys. Rev. **73** (1948) 51.
- 3) C. K. Jen: Phys. Rev. **81** (1951) 198.
- 4) J. R. Eschbach and M. W. P. Strandberg: Phys. Rev. **85** (1952) 24; **82** (1951) 327 A.
- 5) B. F. Burke and M. W. P. Strandberg: Phys. Rev. **90** (1953) 303.
- 6) K. Kondo and T. Oka: to be published.
- 7) T. Oka: to be published.
- 8) T. Nishikawa: The fifth Symposium on Infra-red and Raman Spectra (Chem. Soc. of Japan) Oct. 1958 at Kyoto.

Stark-Zeeman Effects on Asymmetric Top Molecules. Formaldehyde H_2CO .

By Kunitaka KONDO and Takeshi OKA

*Department of Physics, Faculty of Science,
University of Tokyo, Tokyo*

(Received October 3, 1959)

The combined Stark-Zeeman effects for asymmetric top molecules with no accidental degeneracies are studied by perturbation treatments. The theory was applied successfully to the analysis of the experimental results of Stark-Zeeman effect on the microwave spectrum of formaldehyde H_2CO . By the influence of the electric field perpendicular to the magnetic field, split components of the transition $2_{11} \rightarrow 2_{12}$ which, in the magnetic quantum number M , correspond to $\Delta M = \pm 3$ were observed. These components allowed a precise determination of the molecular g -factor for this transition.

§ 1. Introduction

In the study of microwave Zeeman effects for gas molecules, the magnetic and electric fields are often applied simultaneously. The treatment of the combined effects of the two fields is required in some cases¹⁾.

A theory of Stark-Zeeman effects on symmetric top molecules one nucleus of which has a quadrupole moment has been worked out by F. Coester²⁾. As for asymmetric top molecules, the Stark³⁾ and the Zeeman effects⁴⁾ have been studied separately by several authors. The present article is concerned with the Stark-Zeeman effects on asymmetric top molecules with no hyperfine structures. For simplicity, molecules which have accidental degeneracy in their rotational levels are excluded.

§ 2. Theory

The total Hamiltonian of an asymmetric rotor in the external electric and magnetic fields E and H consists of the following terms^{3), 4)}.

$$\mathcal{H} = AJ_x^2 + BJ_y^2 + CJ_z^2, \quad (1a)$$

$$-E \sum_{\lambda=x,y,z} \phi_{E\lambda} \mu_\lambda, \quad (1b)$$

$$-\frac{1}{2}E^2 \sum_{\lambda,\mu=x,y,z} P_{\lambda\mu} \phi_{E\lambda} \phi_{E\mu}, \quad (1c)$$

$$-\frac{1}{2}\mu_0 H \sum_{\lambda,\mu=x,y,z} g_{\lambda\mu} (\phi_{H\lambda} J_\mu + J_\mu \phi_{H\lambda}). \quad (1d)$$

In (1) and in the following discussions, capital subscripts refer to the space-fixed axes or directions, while lower case to the molecule-fixed principal axes of inertia. E and H used as subscripts indicate the directions of

the electric and the magnetic fields respectively.

The term (1a) represents the rotational energy of an asymmetric rotor. A , B and C are the rotational constants related to the principal moments of inertia by $A = \hbar^2/2I_a$, $B = \hbar^2/2I_b$, $C = \hbar^2/2I_c$; J_x , J_y , J_z are components of the total angular momentum vector $\mathbf{J}$ of the molecule. Terms (1d) express the interaction of the molecular rotational magnetic moment with the magnetic field H ; μ_0 is a nuclear magneton; $g_{\lambda\mu}$ are the elements of the molecular g -tensor. The term (1b) is the interaction of the permanent dipole moment of the molecule with the electric field, while (1c) is that of the induced dipole; μ_λ are the components of the polarizability tensor. In (1b), (1c) and (1d) $\phi_{G\lambda}$ ($G=E, H$) are the direction cosines between the space-fixed direction G and the molecule-fixed principal axes of inertia.

The terms (1a) are taken as the unperturbed Hamiltonian, and the terms (1b), (1c) and (1d) as the perturbation. The eigenstates of (1a) are represented in terms of the scheme

$$\Phi(J, \tau, M),$$

in which J and M are the quantum numbers for the rotational angular momentum and its components along the space-fixed Z -axis. The eigenvalues of the rotational energy are specified by the quantum numbers J and τ , and written as

$$W_{J\tau}^0 = \frac{A+C}{2} J(J+1) + \frac{A-C}{2} E_{J\tau}(\kappa), \quad (2)$$

where

$$\kappa = \frac{2B-A-C}{A-C}.$$

In the absence of the external fields, each level is $2J+1$ -fold degenerate with respect to M .

The rotational magnetic moments of ordinary molecules ($^1\Sigma$ in the ground electronic state) are of the order of a nuclear magneton, and the Zeeman energies of these molecules are very small. Hence, the matrix elements of (1d) off-diagonal in J and τ can be neglected. Similarly, the matrix elements of the electric polarization energy (1c) off-diagonal in J and τ can safely be neglected since the polarizabilities of ordinary molecules are 10^{-24} cm³ in order of magnitude. The orientation energy of the permanent dipole moment is always off-diagonal in an asymmetric molecule. The off-diagonal terms of this energy play an important role in the Stark-Zeeman effects.

The total Hamiltonian can then be rewritten in the order of magnitude as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2, \quad (3)$$

where $\mathcal{H}_0$ is the rotational energy (1a), $\mathcal{H}_1$

represents (1b) and $\mathcal{H}_2$ (1c) and (1d).

The perturbation problem can be solved to the order of H and E^2 by the following procedure. First the matrix elements of the Hamiltonian $\mathcal{H}$ off-diagonal in (J, τ) are eliminated to the above order by a transformation;

$$G = S^\dagger \mathcal{H} S \quad (4)$$

and then the transformed Hamiltonian G is diagonalized with respect to the Stark-Zeeman energy.

Eq. (4) is essentially equal to the Van Vleck transformation⁵⁾ and S is given as,

$$S = I + i\lambda S_1 - \frac{1}{2}\lambda^2 S_1^2 \quad (5)$$

where λ is a parameter of smallness, and

$$S_1(J, \tau, M; J', \tau', M') = i \frac{\mathcal{H}_1(J, \tau, M; J', \tau', M')}{W_{J\tau}^0 - W_{J'\tau'}^0}. \quad (6)$$

The transformed Hamiltonian which is to be diagonalized in the manifold of given J and τ is obtained as

$$G = W_{J\tau}^0 + \mathcal{H}_2 + \mathcal{H}_3, \quad (7)$$

where

$$(\mathcal{H}_3)_{MM'} = \sum_{J''\tau''M''} \frac{\mathcal{H}_1(J, \tau, M; J'', \tau'', M'') \mathcal{H}_1(J'', \tau'', M''; J, \tau, M')}{W_{J\tau}^0 - W_{J''\tau''}^0}. \quad (8)$$

The matrix elements of $\mathcal{H}_1$ depend upon the choice of Z -axis. If only electric or magnetic field is applied, or if the two fields are parallel, then Z -axis is to be taken parallel to fields. If the two fields are not parallel, the matrix elements have complex forms. The calculation of matrix elements of the Hamiltonian when the two fields are in arbitrary directions can be simplified by the following consideration of commutation relations.

$\mathcal{H}_1$ and $\mathcal{H}_2$ contain the T -vector operators used in the text-book of Condon and Shortley⁶⁾; they satisfy the following commutation rule with respect to J referred to the space-fixed axes,

$$[J, T] = -[T, J] = -iJ \times \mathcal{J}. \quad (9)$$

Eq. (9) is written in a dyadic form, where $\mathcal{J}$ is the unit dyadic.

Electric and magnetic dipole moments referred to the space fixed axes as well as the direction cosines are T operators. The matrix elements of T can be expressed as

$$(J, \tau, M | T | J', \tau', M') = (J, \tau | T | J', \tau') (T)_{JM; J'M'}. \quad (10)$$

Hence the dependence of the matrix T on M is given by that of $(T)_{JM; J'M'}$. The components of T in the space-fixed direction $G(\phi_{XG}, \phi_{YG}, \phi_{ZG})$ are obtained by

$$(T_G)_{JM; J'M'} = \sum_{F=X,Y,Z} \phi_{FG} (T_F)_{JM; J'M'}, \quad G=E, H,$$

where⁶⁾,

$$\left. \begin{aligned} (T)_{JM, J+1M\pm 1} &= \mp \frac{1}{2} \sqrt{(J \pm M + 1)(J \pm M + 2)} (i \pm ij) \\ (T)_{JM, JM\pm 1} &= \frac{1}{2} \sqrt{(J \mp M)(J \pm M - 1)} (i \pm ij) \\ (T)_{JM, J-1M\pm 1} &= \pm \frac{1}{2} \sqrt{(J \mp M)(J \mp M - 1)} (i \pm ij) \\ (i, j, k \text{ are unit vectors along } X, Y, Z \text{ axes.}) \end{aligned} \right\} \quad (11)$$

$$\left. \begin{aligned} (T)_{JM, J+1M} &= \sqrt{(J+1)^2 - M^2} k, \\ (T)_{JM, JM} &= Mk, \\ (T)_{JM, J-1M} &= \sqrt{J^2 - M^2} k, \end{aligned} \right\}$$

The matrix elements of the direction cosines are,

$$\left. \begin{aligned} (J, \tau | \phi_{G\lambda} | J, \tau') &= \frac{(\phi_{G\lambda})_{J, \tau; J, \tau'}}{2J(J+1)}, \\ (J, \tau | \phi_{G\lambda} | J', \tau') &= \frac{(\phi_{G\lambda})_{J, \tau; J', \tau'}}{2J^* \sqrt{4J^{*2} - 1}}, \end{aligned} \right\} \quad (12)$$

where $J' = J \pm 1$, and J^* represents the larger of J and J' .

For the magnetic moment operator m ,

$$(J, \tau | m | J, \tau) = \mu_0 g_{J\tau} \quad (13)$$

in which $g_{J\tau}$ is the molecular g -factor for the J_τ 'th rotational level.

The matrix components of the permanent and the induced electric dipole moment can be obtained by using those of the direction cosines.

If the symmetry properties discussed in reference (3) are taken into account together with the above considerations, the matrix elements of G are calculated as

$$\begin{aligned} G_{MM'} &= W_{J\tau}^0 \delta_{MM'} - \mu_0 g_{J\tau} H(T_H)_{J, M; J', M'} \\ &+ \sum_{\lambda=x, y, z} \frac{E^2}{2J+1} \sum_{\tau'} \left[\left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J-1\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) \frac{^{\lambda}S_{J\tau; J-1\tau'}}{J(2J-1)} \sum_{M''} (T_E)_{J, M; J-1, M''} (T_E)_{J-1, M''; J, M'} \right. \\ &+ \left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) \frac{^{\lambda}S_{J\tau; J\tau'}}{J(J+1)} \sum_{M''} (T_E)_{J, M; J, M''} (T_E)_{J, M''; J, M'} \\ &\left. + \left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J+1\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) \frac{^{\lambda}S_{J\tau; J+1\tau'}}{(J+1)(2J+3)} \sum_{M''} (T_E)_{J, M; J+1, M''} (T_E)_{J+1, M''; J, M'} \right] \quad (14) \end{aligned}$$

where $^{\lambda}S_{J\tau; J'\tau'}$ are the transition strengths^{7,8)}. Eq. (14) is valid for arbitrary directions of the two fields.

There are two typical cases of fields directions; one the parallel and the other the crossed fields case.

A. Parallel fields case

Z -axis is chosen in the direction of fields; G is diagonal in M , and consists of the rotational energy, the Zeeman energy $-\mu_0 g_1 M H$, and the Stark energy given in reference (3). Each Stark component of transitions is split into two by the influence of the magnetic fields. Selection rules and the transition intensities are not altered by the fields.

B. Crossed fields case

When one of the two fields is much stronger than the other, Z -axis may be taken parallel to the stronger field. Some convenient approximations such as the expansion is power series of the ratio of the weaker to the stronger field may be employed. Here the intermediate fields case will be discussed. If Z -axis is taken parallel to the magnetic field, the matrix elements of G are obtained as;

$$\begin{aligned} G_{MM} &= W_{J\tau}^0 - \mu_0 g_{J\tau} M H \\ &+ \sum_{\lambda=x, y, z} \frac{E^2}{2(2J+1)} \sum_{\tau'} \left[\left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J-1\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) ^{\lambda}S_{J\tau; J-1\tau'} \frac{J(J-1)+M^2}{J(2J-1)} \right. \\ &+ \left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) ^{\lambda}S_{J\tau; J\tau'} \frac{J(J+1)-M^2}{J(J+1)} \\ &\left. + \left(\frac{\mu_\lambda^2}{W_{J\tau}^0 - W_{J+1\tau'}^0} - \frac{P_{\lambda\lambda}}{2} \right) ^{\lambda}S_{J\tau; J+1\tau'} \frac{(J+1)(J+2)+M^2}{(J+1)(2J+3)} \right], \quad (15) \end{aligned}$$

$$\begin{aligned}
 G_{M, M \pm 2} = & -E^2 \frac{\sqrt{[J(J+1)-M(M \pm 1)][J(J+1)-(M \pm 1)(M \pm 2)]}}{4(2J+1)} \\
 & \times \sum_{\lambda=x, y, z, \tau'} \left[\left(\frac{\mu_{\lambda}^2}{W_{J\tau}^0 - W_{J-1\tau'}^0} + \frac{P_{\lambda\lambda}}{2} \right) \frac{\lambda S_{J\tau; J-1\tau'}}{J(2J-1)} \right. \\
 & + \left(-\frac{\mu_{\lambda}^2}{W_{J\tau}^0 - W_{J\tau'}^0} + \frac{P_{\lambda\lambda}}{2} \right) \frac{\lambda S_{J\tau; J\tau'}}{J(J+1)} \\
 & \left. + \left(\frac{\mu_{\lambda}^2}{W_{J\tau}^0 - W_{J\tau'}^0} + \frac{P_{\lambda\lambda}}{2} \right) \frac{\lambda S_{J\tau; J+1\tau'}}{(J+1)(2J+3)} \right]. \quad (16)
 \end{aligned}$$

All other elements vanish, hence the Hamiltonian matrix is reduced into two parts, one for

$$M = -J, -J+2, \dots, J,$$

and the other for

$$M = -J+1, -J+3, \dots, J-3, J-1.$$

The exact solutions of the eigenvalue problem are not obtained except some special cases (for example, $J=1$ and 2), but some informations about the selection rules and the number of split components of transitions are obtained. Under crossed fields condition, only states whose quantum numbers M differ by even numbers are mixed. Therefore, when the oscillating electric field which induces the electric dipole transition is parallel to the magnetic field, selection rules and the number of all possible split lines are,

$$\left. \begin{aligned}
 \Delta M = 0, & \quad n = 2J+1, \\
 \Delta M = \pm 2, & \quad n = 2(2J-1), \\
 \vdots \\
 \Delta M = \pm 2k, & \quad n = 2[2(J-k)+1], \\
 \vdots \\
 \Delta M = \pm 2J, & \quad n = 2.
 \end{aligned} \right\} \quad (17)$$

total number = $2J(J+2)+1$.

When the oscillating electric field is perpendicular to the static magnetic field and parallel to the electric field,

$$\left. \begin{aligned}
 \Delta M = \pm 1, & \quad n = 4J, \\
 \Delta M = \pm 3, & \quad n = 4(J-1), \\
 \vdots \\
 \Delta M = \pm(2k-1), & \quad n = 4(J-k+1), \\
 \vdots \\
 \Delta M = \pm(2J-1), & \quad n = 4,
 \end{aligned} \right\} \quad (18)$$

total number = $2[J(J-1)+2]$.

Relative intensities of lines corresponding to various values of M and ΔM depend upon the relative intensities of the electric and magnetic fields.

§ 3. Experiment and Result

An experimental study of Stark-Zeeman effects was carried out on the microwave spectrum of formaldehyde H_2CO under the strong, intermediate, and weak electric field conditions. The hyperfine structure in the spectrum of formaldehyde⁹⁾ was not observed in the present experiment and therefore they are neglected in the following discussions. Asymmetry of this molecule is very small. The rotational energy levels of such a slightly asymmetric rotor consist of K -type doublets, and they give the largest contribution to the second order Stark effect.

Table I. Eigenfunctions and energy levels of the K -type doublet, $J=1$ and $K_1=1$.

Level (J_τ)	$W_{J\tau}^0$	M	Wave function	Stark-Zeeman energy
1_0	$A+C$	1	$p_0\psi_{01}+q_0\psi_{0,-1}$	$-\beta_0+\sqrt{\alpha_0^2+\beta_0^2}$
		0	ψ_{00}	$-\gamma_0$
		-1	$-q_0\psi_{01}+p_0\psi_{1,-1}$	$-\beta_0-\sqrt{\alpha_0^2+\beta_0^2}$
1_1	$A+B$	1	$p_1\psi_{11}-q_1\psi_{1,-1}$	$\beta_1+\sqrt{\alpha_1^2+\beta_1^2}$
		0	ψ_{10}	γ_1
		-1	$q_1\psi_{11}+p_1\psi_{1,-1}$	$\beta_1-\sqrt{\alpha_1^2+\beta_1^2}$

$$\alpha_\tau = |g_\tau \mu_0 H|$$

$$\beta_\tau = \left[\frac{1}{8(B-C)} + (-1)^{1+\tau} \frac{7}{80(B+C)} \right] \mu^2 E^2$$

$$\gamma_\tau = \left[\frac{1}{4(B-C)} + (-1)^{1+\tau} \frac{3}{56(B+C)} \right] \mu^2 E^2$$

$$p_\tau = \frac{1}{\sqrt{2}} \left[1 + \frac{\alpha_\tau}{\sqrt{\alpha_\tau^2 + \beta_\tau^2}} \right]^{1/2}$$

$$q_\tau = \frac{1}{\sqrt{2}} \left[1 - \frac{\alpha_\tau}{\sqrt{\alpha_\tau^2 + \beta_\tau^2}} \right]^{1/2}$$

$$\phi_{\tau, M} \equiv \psi(J=1, \tau, M)$$

The experimental apparatus is the same as reported in the preceding paper¹. The d.c. electric field was applied by a usual Stark electrode, and the magnetic field was produced along the length of the wave guide by a solenoidal coil surrounding the wave guide. Hence the theory of the crossed fields case should be applied. The microwave electric field, which causes the dipole transitions, is parallel to the static electric field, and the selection rules are

$$\Delta M = \pm 1, \pm 3, \dots, \pm(2J-1),$$

as was indicated in Eq. (18).

The observed absorption lines of H_2CO correspond to the direct transitions between K -type doublets, $1_{10} \leftarrow 1_{11}$ (4829, 78 Mc) and $2_{11} \leftarrow 2_{12}$ (14488, 34 Mc). The number of possible split lines in this case are

$$n = 2(J-k), \quad \text{for } \Delta M = \pm(2k+1), \quad (19)$$

and the total number is $J(J+1)$. This is easily seen if we notice that the frequencies of the transitions $M' \leftarrow M$ and $-M \leftarrow -M'$ coincide, provided that the g -factors for the

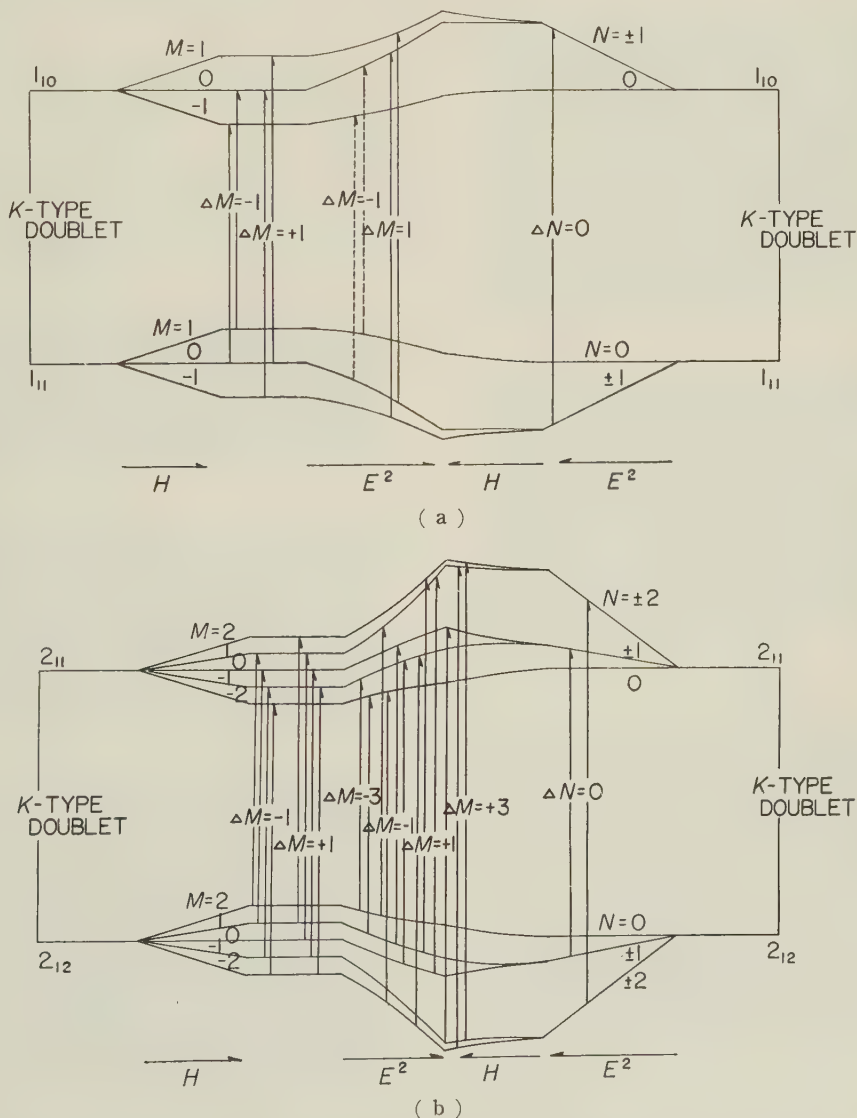


Fig. 1. (a) Stark-Zeeman effects on the K -type doublet $J=1, K-1=1$. Solid lines represent allowed transitions; dotted lines in intermediate cases indicates forbidden transitions in the strong electric field limit. (b) Stark-Zeeman effects on the $J=1, K-1=1$ K -type doublet. Solid lines indicate all allowed transitions.

two levels are equal.

$1_{10} \leftarrow 1_{11}$;

The initial secular equations of sixth order reduces, in this case, to two linear and two quadratic equations. The wave functions and energies are given in Table I.

Fig. 1(a) shows the behaviour of energy levels when the fields are applied, where N is the quantum number of a component of $\mathbf{J}$ along the electric field. The intensity of the line corresponding to the $\Delta M=1$ transition becomes stronger when the electric field is

increased and coincides with the transition $\Delta N=0$ in the limiting strong electric field case, while the line corresponding to the $\Delta M=-1$ transition becomes weaker and coincides with the forbidden transition $\Delta N=\pm 1$ in the strong

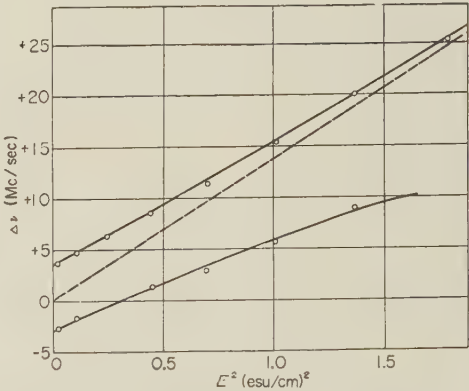
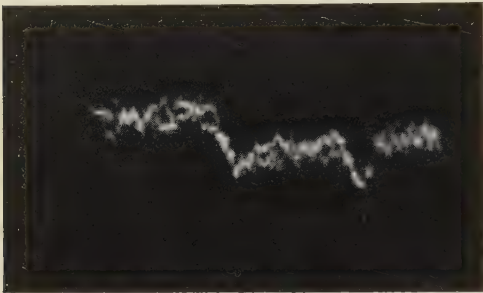
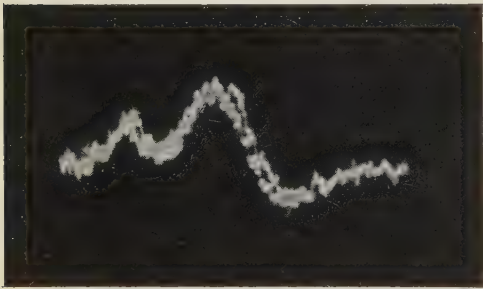


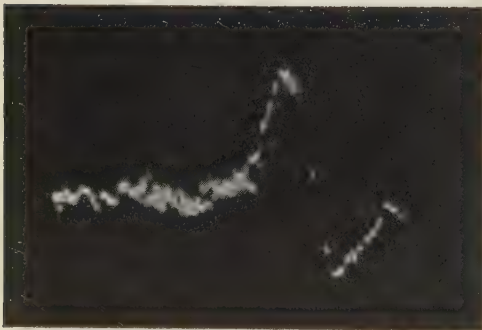
Fig. 3. Comparison of theory and measurements of Stark-Zeeman effects in the $1_{10} \leftarrow 1_{11}$ transition of H_2CO . The dotted line indicates the pure Stark effect.



(a)

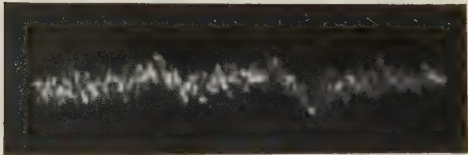


(b)

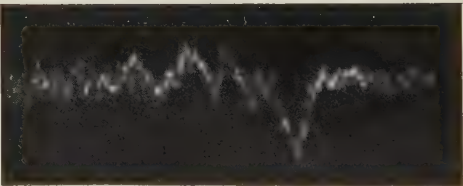


(c)

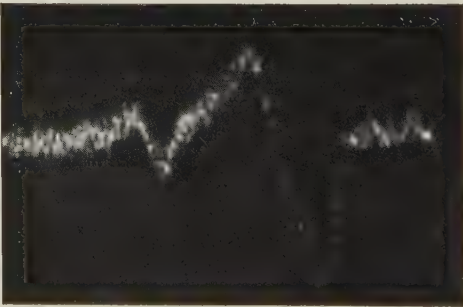
Fig. 2. The Stark-Zeeman patterns of the transition $1_{10} \leftarrow 1_{11}$ of H_2CO . (a) A weak electric field case; $E=50$ V/cm, $H=1750$ oe. (b) An intermediate case; $E=150$ V/cm, $H=1750$ oe. (c) A strong electric field case; $E=250$ V/cm, $H=1750$ oe.



(a)



(b)



(c)

Fig. 4. The Stark-Zeeman patterns of the transition $2_{11} \leftarrow 2_{12}$ of H_2CO . (a) A weak electric field case; $E=228$ V/cm, $H=1980$ oe. (b) An intermediate case; $E=478$ V/cm, $H=1980$ oe. (c) The pure Stark effect; $E=348$ V/cm, $H=0$.

field limit. This situation is well shown in Fig. 2, in which the Stark-Zeeman patterns of the $1_{10} \leftarrow 1_{11}$ line under the strong, intermediate, and weak electric fields are shown.

From the best fit of the calculated frequencies to the observed ones (Table II), the g -value of these levels,

$$g_1 = 1.529 \pm 0.05 \quad (20)$$

and the electric dipole moment along the symmetry axis,

$$\mu_a = 2.323 \pm 0.015 \quad \text{Debye units}, \quad (21)$$

were obtained.

$2_{11} \leftarrow 2_{12}$:

The calculation of the analytical solutions of eigenvalue problem for this case is straightforward and tedious. No further analysis is

Table II. Stark-Zeeman effect for the $1_{10} \leftarrow 1_{11}$ transition of H_2CO . The unit intensity is that of the $\Delta M = 1$ transition in the pure Zeeman case. $H = 2805 \pm 20$ oe.

ΔM	E	$\Delta\nu$ (calc)	$\Delta\nu$ (obs)	Intensity (calc)
-1	52.1 V/cm	-3.22 Mc/sec	-3.27 Mc/sec	0.97
	104.2	-2.24	-2.43	0.88
	156.3	-1.04	-1.06	0.73
	208.4	-0.82	0.74	0.55
	260.5	2.80	2.90	0.38
1	312.6	5.31	5.39	0.25
	52.1	3.29	3.27	1.03
	104.2	4.23	4.19	1.12
	156.3	5.81	5.71	1.27
	208.4	7.96	7.98	1.45
1	260.5	10.93	11.04	1.62
	312.6	14.86	14.94	1.75

Table III. Stark-Zeeman effect for the transition $2_{11} \leftarrow 2_{12}$ of H_2CO , when $H = 1980 \pm 20$ oe and $E = 490 \pm 3$ V/cm. (The unit intensity is that of the $M = -1 \leftarrow -2$ transition in the pure Zeeman effect.)

Transition	ΔM	$\Delta\nu$ (obs)	$\Delta\nu$ (calc)	Intensity (calc)
$1 \leftarrow -2, 2 \leftarrow -1$	3	5.96 Mc/sec	5.96 Mc/sec	2.76
$1 \leftarrow 0, 0 \leftarrow -1$	1	4.40	4.40	1.78
$-1 \leftarrow -2, 2 \leftarrow -1$	1	3.38	3.34	1.09
$0 \leftarrow -1, -1 \leftarrow 0$	-1		1.78	0.09
$-2 \leftarrow -1, 1 \leftarrow 2$	-1	1.66	1.56	0.10
$-2 \leftarrow -1, -1 \leftarrow 2$	-3	1.06	1.08	0.37

described here, although some numerical values of the frequencies corresponding to the experimental values of E and H is given below.

Fig. 1(b) shows energy levels and selection rules in several cases. Under the intermediate fields condition, transitions corresponding to $\Delta M = \pm 3$, which are forbidden in the limiting pure Zeeman case, are expected. Stark-Zeeman patterns of the line shown in Fig. 4 are well interpreted by considering these transitions.

At the fields of $E = 490 \pm 2$ V/cm and $H = 1980 \pm 35$ oe, five components were observed. The g -value and the electric dipole moment were determined so that the calculated frequencies for these fields intensities may fit best to the observed values (Table III).

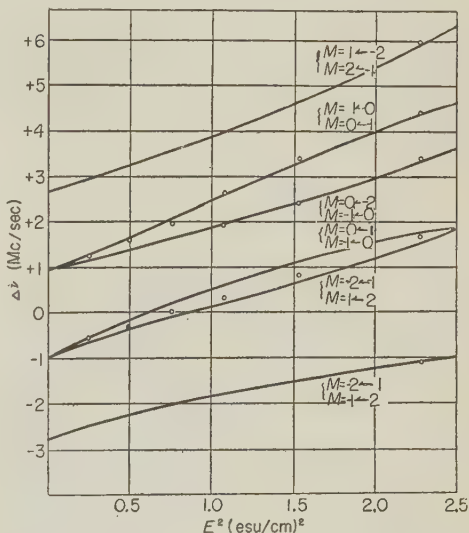


Fig. 5. Frequency of all Stark-Zeeman components of H_2CO $2_{11} \leftarrow 2_{12}$ transition as a function of electric field strength. Magnetic field is 1980 oe. Solid lines represent the theoretical values computed so that they may fit best the observed values at $E = 1.63 \pm 0.01$ esu/cm.

The results are

$$g_2 = 0.610_8 \pm 0.012, \quad (22)$$

$$\mu_a = 2.339 \pm 0.015 \quad \text{Debye units}. \quad (23)$$

Here the value of g -factor is more precise than the one determined by the pure Zeeman effect. This is due to the large splittings of components corresponding to $\Delta M = \pm 3$ together with the increased number of split lines. If advantage is taken of these facts, the g -values which are not large enough to be obtained from the pure Zeeman effect may possibly be

determined by the Stark-Zeeman effect in the crossed fields case.

Observed frequencies at various field intensities show good agreements with the frequencies calculated with the values of (22) and (23). (Fig. 5)

With the values of (20) and (22), aa -component of the g -tensor g_{aa} can be obtained as

$$g_{aa} = \frac{5g_1 - 2g_2}{3} = 2.906 \pm 0.05.$$

This agrees with the value given in reference (1) within the experimental error.

Acknowledgement

The authors are indebted to Professor Koichi Shimoda for his kind guidance and encouragement throughout the course of this investigation. They are also grateful to Mr. Akira Miyahara for his helpful suggestions in the experimental detail, and to Mr. Tadao Shimizu for his checking of the formula appearing in this manuscript.

References

- 1) K. Kondo, H. Hirakawa, A. Miyahara, T. Oka and K. Shimoda: to be published.
- 2) F. Coester, Phys. Rev. **77** (1956) 454.
- 3) S. Golden and E. B. Wilson, Jr.: J. Chem. Phys. **16** (1948) 669.
- 4) B. F. Burke and M. W. P. Strandberg: Phys. Rev. **90** (1953) 303. i.b.i.d. **90** (1953) 308A.
- 5) E. C. Kemble: *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Co., New York, 1937) 394. J. H. Van Vleck: Phys. Rev. **33** (1929) 467. O. M. Jordahl: Phys. Rev. **45** (1934) 87.
- 6) E. U. Condon and G. H. Shortley: *Theory of Atomic Spectra* (Cambridge Univ. Press, Cambridge, 1951).
- 7) P. C. Cross, R. M. Hainer and G. W. King: J. Chem. Phys. **12** (1944) 210.
- 8) C. H. Townes and A. L. Shawlow: *Microwave Spectroscopy* (Mc-Graw Hill Book Co., New York, 1955).
- 9) H. Takuma, T. Shimizu and K. Shimoda: J. Phys. Soc. Japan **14** (1959) 1595. See also ref. 1).

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

Luminescences from KBr/KI Single Crystals*

By Masao TOMURA and Yôzo KAIFU

Institute of Polytechnics of Osaka City University, Osaka

(Received August 24, 1959)

Luminescences from KBr/KI single crystals were observed. Two kinds of them were found. The one was attributed to localized I^- ions and the other to aggregated I^- ions. They suffered Stokes shift and were quenched thermally at room temperature. In cases of large concentration of KI, both emissions coincided with each other, while a new emission appeared which was coincident with that observed in pure KI crystals. And the nature of exciton in alkali halide was discussed.

§ 1. Introduction

It is well known that no photoconductivities and no edge luminescences have been observed with irradiation of light in the first fundamental absorption band of alkali halides. The process of dissipation of exciton energy has not been yet clarified. One will infer

that the exciton has a radiationless configuration and dissipates its energy as phonons to the lattice. Alternatively, Seitz¹⁾ has supposed that the dissipation of the exciton energy takes place in the course of migration of the exciton through the crystal. Although the exciton itself has a radiative configuration, it wanders in the crystal and interacts with impurities or defects, dissipating its energy before radiating its own edge luminescence.

* Reported at the meetings of the Phys. Soc. Japan (Oct. 1957 and Apr. 1958).

On the other hand, luminescences which suffered Stokes shift were observed under irradiation in the fundamental band in NaI²⁾ and KI³⁾, and they were attributed to the annihilation of the exciton itself. According to the exciton theory⁴⁾, there exist exciton bands in ionic crystals, and after the excitation to these bands the edge luminescence should appear at the wave length a little longer than the peak of exciton absorption band. For an emission which has received Stokes shift, however, it must be necessary that a localized exciton is formed just after the absorption of light. If the moving exciton becomes self-trapped at a particular atom, it will be transformed into the localized exciton which is able to emit a luminescence shifted to a much longer wave length.

Now, in a dilute solid solution of KI in KBr, transfer of electronic excitation energy from an excited I⁻ ion is impossible, since the I⁻ ion is not in resonance with its surroundings. In this case we are able to determine whether the excited I⁻ ion is radiative or non-radiative. Since the immediate environment of the I⁻ ion is almost same in both cases of KBr/KI and KI, we are able to infer whether the exciton of KI has a radiative configuration or not.

If the excited I⁻ ion in KBr has the emissive nature, it is very interesting to follow after changes of the emission from the I⁻ ion while the I⁻ ion concentration becomes large. We may obtain relations between the luminescences from the localized I⁻ ion and the edge luminescence of KI.

Here, the luminescences from alloyed KBr/KI single crystals were observed for various concentrations of I⁻ ion in order to obtain knowledges of the nature of exciton in KI.

§2. Absorption by I⁻ ion in KBr/KI

Alloyed single crystals of KBr/KI were prepared by the usual Kylopoulos method. Concentrations of I⁻ ion were chemically analysed only for specimens of lower concentrations with the following process. KI in the alloyed crystal is converted to KIO₃ by oxidizing with Br, and then I is made free by adding KI to KIO₃. The freed I is measured by iodometry. Thus the quantity of six times of the initial I in the crystal can be determined. For the specimens of

higher concentration of I⁻ ion than 1×10^{-1} mol, the denoted concentrations are mentioned as the mixing ratio of KI and KBr.

When a KBr crystal contains a small amount of KI, some of Br⁻ ions are replaced substitutionally by I⁻ ions, which eventually distribute randomly in the host crystal.

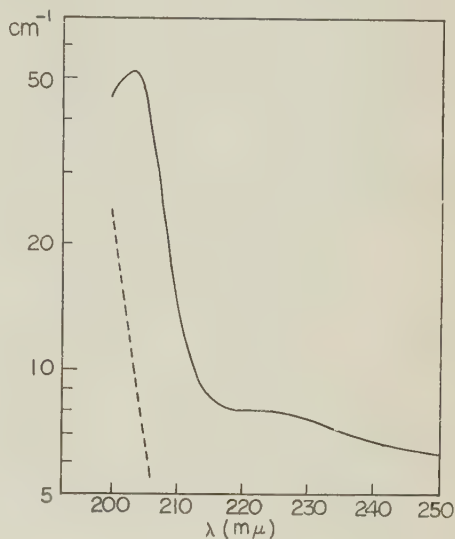


Fig. 1. The optical absorption coefficient of a KBr/KI single crystal at room temperature. The concentration of KI is 2.0×10^{-4} mol. The dotted curve shows the absorption coefficient of a pure KBr single crystal.

Then the Greek band due to the I⁻ ion, that is, the absorption band due to the localized exciton around the I⁻ ion, appears in the long wave length tail of the exciton absorption band of KBr. Fig. 1 shows the optical absorption band of a KBr/KI single crystal at room temperature. Because of rather large amounts of stray light in the Beckman monochromator used, the measurements were not so much accurate. The absorption band due to the localized I⁻ ion appears at 203 m μ and the half width of the band is about 0.19 eV. Neglecting the amount of the aggregated I⁻ ion mentioned later, the oscillator strength of the absorption band is about 0.02. The position of the peak of the band shifts to the longer wave length side when the concentration of I⁻ ion becomes larger. For instance, the peak shifts to 206 m μ for the specimen of 5.8×10^{-4} mol KI concentration. Extrapolating the wave length of the peak to the case of zero I⁻ ion concentration, we obtain 201

$m\mu$. The difference of photon energies between the exciton absorption band of KBr and the extrapolated absorption band is 0.42 eV, and is larger than the difference of electron affinities of Br and I atoms, that is 0.35 eV. Perhaps the fact that the ionic radius of I^- ion is larger than that of Br^- ion will be a main cause of the inaccordance. The peak of the absorption band shifts also to the longer wave length side by a few $m\mu$ under the 30~45% plastic deformation.

As shown in Fig. 1, a slight hump is observed at about 225 $m\mu$, that is, the wave length a little longer than the peak of the exciton absorption band. The absorption coefficient of this band is the order of 1 cm^{-1} and varies with the formation and quenching speeds in the procedure of preparing the crystal. This absorption band is hardly attributed to any impurities. Because both KI and KBr crystals which are made of the same reagents as that used for the alloyed crystal do not show any appreciable absorption bands of impurities. The above slight absorption band appears only in the alloyed crystal of KBr/KI.

In the X-ray rotation photograph of the alloyed KBr/KI crystal⁽⁵⁾, two types of pattern appear. One is due to alloyed KBr/KI and the other is ascribed to pure KI. The latter pattern shows no shape for a large single crystal, but seems to have a shape for a small crystal. Thus the existence of aggregated KI which is as small as 1μ in size is found. The slight absorption hump at 225 $m\mu$ may be attributed to these small aggregation of KI as mentioned later.

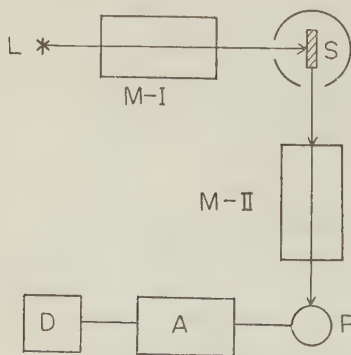


Fig. 2. The arrangement of apparatuses. L: hydrogen discharge tube, M-I and M-II: quartz monochromator, S: specimen, P: photomultiplier, A: amplifier and D: detecting meter.

§ 3. Luminescences from I^- ion in KBr/KI

The measurements of luminescences from KBr/KI single crystals were carried out by the usual method as shown in Fig. 2. Energies of incident lights on specimens were measured by a 1P 28 photomultiplier. The spectral sensitivity of the photomultiplier was calibrated with sodium salicylate below 300 $m\mu$ and with the data in the catalogue above 300 $m\mu$. The spectral transmission of the monochromator II which resolved emitted luminescences was calibrated to make sure the real shape of the emission band. The band pass of the monochromator I is 5 $m\mu$ at 225 $m\mu$ and that of the monochromator II is

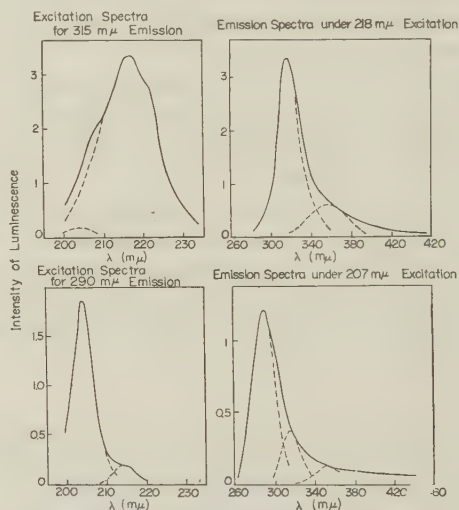


Fig. 3. The emission and excitation spectra for the specimen of 2.9×10^{-2} mol KI concentration.

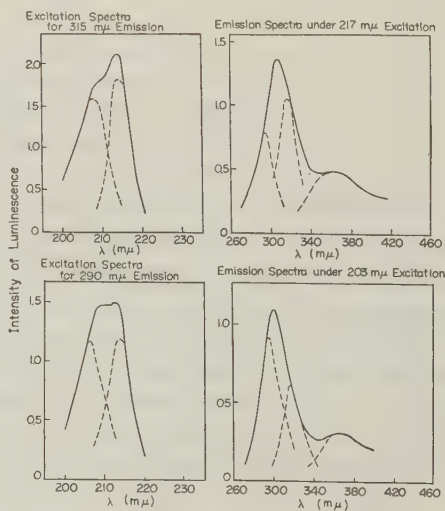


Fig. 4. The emission and excitation spectra for the specimen of 3.0×10^{-1} mol KI concentration.

10 $m\mu$ at 350 $m\mu$ respectively. The source of the exciting light is a hydrogen discharge tube of hot cathode type. Size of the specimens were about $1.5 \times 1.0 \times 0.2 \text{ cm}^3$.

Under irradiations of lights in the absorption bands due to a single localized I^- ion and aggregated I^- ions, emissions were observed respectively, at the liquid oxygen temperature. Their intensities varied both proportionately with intensities of the incident lights, and though the spectral intensity of the incident light was not held constant, the intensities of the emissions per energy of incident light were obtained by calculations after the measurements.

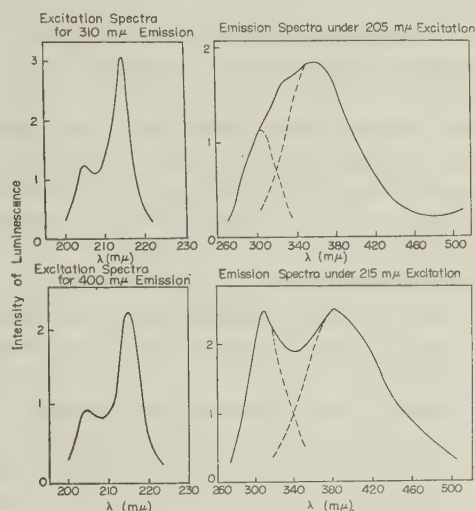


Fig. 5. The emission and excitation spectra for the specimen of 7.0×10^{-1} mol KI concentration.

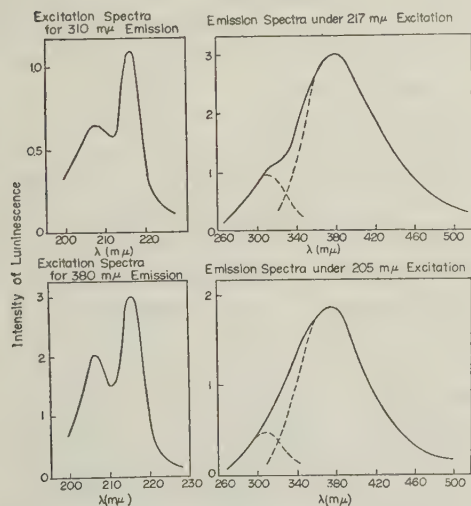


Fig. 6. The emission and excitation spectra for the specimen of 8.5×10^{-1} mol KI concentration.

Results are shown in Figs. 3~7 for various concentrations of I^- ion. The ordinate scale is arbitrary, but the relative intensities of the emissions are maintained to be roughly equal. As the emissions were all thermally quenched at room temperature, the measurements were carried out at the liquid oxygen temperature at which the emissions were almost saturated. The quantum yields of the luminescences were not measured, but they were all estimated as one tenth of unity in the order of magnitude in the reference to the emission of KI/TiI . Both emission and excitation bands overlap with each other respectively, so the bands are shown as separated roughly with dotted curves in the figures.

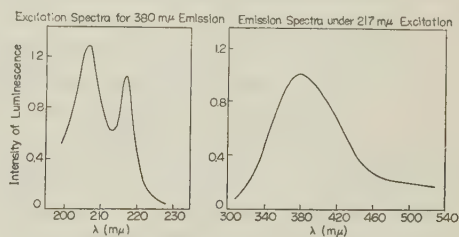


Fig. 7. The emission and excitation spectra for pure KI.

While the I^- ion concentration is as low as $10^{-4} \sim 10^{-2}$ mol, the emissions due to the absorptions by the localized I^- ion and aggregated I^- ions have the peak at 290 $m\mu$ and 315 $m\mu$ respectively. (See Fig. 3.) The excitation spectrum for the former emission is normal in shape and in position, that is, the shape is of bell type and the position of the peak lies at the same position as that of the absorption band due to the localized I^- ion. The latter excitation spectrum, however, is very much deformed in shape and lies on the whole in a wave length region a little longer than the exciton absorption peak of KI at the liquid oxygen temperature. In view of these circumstance and the results of the X-ray analysis, we may infer that the above excitation spectrum corresponds to the slight hump of the absorption band at 225 $m\mu$ observed at room temperature and it is due to the aggregates of KI which deposited in small size in the host crystal. The exciton absorption band of KI of very small size will lie in a wave length region longer than that of KI of large size, because of smaller dipole-dipole interaction energy. The deformed shape of

the excitation spectrum may be attributed to non-uniform size of the aggregation of KI.

When the I^- ion concentration becomes larger, the position of the above two emissions approach with each other. For instance, both emissions almost coincide with each other at $305\text{ m}\mu$ just like a single band in the case of 3×10^{-1} mol KI concentration. At the same time, the excitation spectra for both emissions become similar to each other in shape and position. In this case, however, the excitation bands as well as the emission bands seem to be separated into components. The deformed shape of the excitation spectrum for the emission band at $315\text{ m}\mu$ alters itself and the long wave length side of the spectrum becomes very sharp against the case of the lower I^- ion concentration.

In the case of 7×10^{-1} mol KI concentration, the above two emission bands can be hardly separated. As for the excitation spectra, they become much more likewise as each other in shape and position than in the case of 3×10^{-1} mol KI concentration. (See Fig. 5).

On the other hand, a new emission band peaking at $360 \sim 380\text{ m}\mu$ appears in the case of 2.9×10^{-2} mol KI concentration. It can be hardly observed in cases of much lower concentration of I^- ion. The larger the concentration of I^- ion, the higher the intensity of the emission, and at last it overcomes the intensity of the emission at $305\text{ m}\mu$ which is found to be a coincident emission from both localized I^- ion and the aggregated I^- ions. (See Fig. 6). This new emission is coincident with the emission³⁾ observed in pure KI.

Even in the case of 8.5×10^{-1} mol KI concentration, the emission at $305\text{ m}\mu$ can be detected a little. In the cases of 7×10^{-1} mol and 8.5×10^{-1} mol KI concentrations, shapes and positions of all the excitation spectra resemble with each other.

In Fig. 7 the emission from a pure KI crystal is shown. The band at $305\text{ m}\mu$ disappears completely. The emission band peaking at $380\text{ m}\mu$ is the almost same one as that observed by Teegarden³⁾. The position of the peak shifts in the region between $360\text{ m}\mu$ and $400\text{ m}\mu$ for various specimens.

§ 4. Discussion

The results shown in Fig. 3 show clearly the appearance of the luminescence from the

I^- ion in alloyed KBr/KI. As the emission suffers the Stokes shift and shows the nature of thermal quenching, the I^- ion is just similar to a normal activator in a luminescent material. From the fact that the localized exciton around the I^- ion has a radiative configuration, the configuration of the exciton of pure KI may be inferred as also radiative, since the immediate neighbourhoods of the I^- ion are almost the same in KBr/KI and KI.

As shown in Fig. 3, the shape of the excitation spectrum for the emission at $290\text{ m}\mu$ which comes from the localized I^- ion is of bell type. The absorption coefficient of the specimen of 2.9×10^{-2} mol KI concentration was not measured, however, comparing to that of the specimen of 2×10^{-4} mol KI concentration it will be so large that almost all of the incident light is absorbed in the middle region of the absorption band. Accordingly, we should expect the shape of the excitation band as flat. The cause of this discrepancy may be attributed to the wide band pass of the monochromator I.

In the cases of higher concentration of KI, the configuration around the I^- ion must approach that of pure KI. Then also the electronic structure of the localized exciton at the I^- ion may approach that of the exciton in pure KI, so the position of the emission from the localized exciton may shift to that of the edge luminescence, that is, about $220\text{ m}\mu$. As Figs. 4, 5 and 6 show, it is found that the emission at $290\text{ m}\mu$ does not shift to the shorter wave length side, but to the rather longer wave length of $305\text{ m}\mu$ with increase of KI concentration.

As the aggregated I^- ions also emit the luminescence which is suffered with Stokes shift, the electronic excitation at the aggregated I^- ions is localized on them, though the aggregation is made of only KI which should emit the edge luminescence. As mentioned in § 2 the size of the aggregated KI is so small as 1μ in the order of magnitude, the nature of the excited state of the aggregation differs from that of the normal exciton in the crystal of large size. Heller and Marcus⁹⁾ have pointed out that the dipole-dipole interaction energy is very sensitive to the range of the lattice sum in the calculation of the energy. Vavilov's⁷⁾ experiment will support

these considerations. He has observed unusually the well developed luminescence phenomena in very fine capillaries, using dye solutions which do not display such effects in bulk. Thus the excitation in the aggregated KI of very small size may be localized and display the emission which suffered Stokes shift, though the constituents in the aggregation is the same as that in the bulk of KI.

When the KI concentration becomes large in the alloyed crystal, as the lattice spacing around the I^- ion becomes large, the position of the emission band from the localized I^- ion shifts to the longer side. At the same time the size of the aggregation of KI grows, so the position of the emission from it shifts to the shorter wave length side, because of growth of the aggregation. The larger is the size of the aggregation, the larger is the dipole-dipole interaction, resulting that the electronic structure becomes similar to that of the exciton in pure KI. Then in the case of higher concentration of KI, both emissions from the localized I^- ion and aggregated I^- ions will coincide with each other at 305 m μ . The fact that the shape and position of the excitation spectra shown in Figs. 5 and 6 are very much similar to that of pure KI in Fig. 7 may also show that the electronic structures around the localized I^- ion and the aggregated I^- ions both approach to that of the exciton in pure KI.

In the next place, the appearance of the emission at 360~380 m μ in the cases of higher concentration of I^- ion is explained from the results by Tomura⁹⁾ on the exciton induced luminescence of KI/TlI. He found two emissions under excitation of light in the exciton absorption band. One is the induced emission from Tl^+ ion and the other is coincident with the above mentioned emission at 360~380 m μ . From the intensities of both emissions, he estimated the effective number of the center which displayed the latter emission as $10^{16}/\text{cm}^3$ with the reference to the Tl^+ ion concentration. Accordingly, the latter emission can be hardly attributed to any center of intrinsic type, but to some impurities or defects in the host KI crystal. The energies absorbed by the localized and aggregated I^- ions are transferred to these impurities, giving rise to the above emission. The higher is the concentration of the I^- ion, the larger is the

probability of the energy transfer to the impurities, while the self emissions at the localized and aggregated I^- ions decrease.

In Fig. 6 it is shown that the emission at 305 m μ , that is, the emission from the localized configuration around the I^- ion, is found to a small amount even in the specimen of very high I^- ion concentration such as 8.5×10^{-1} mol. In these alloyed crystal, however, some of I^- ions might be localized separately as a result of non-uniform distribution, and give rise to the emission of localized type. In this case, however, the shape and position of the excitation spectrum for this emission are just similar to that of the excitation spectrum shown in Fig. 7. This fact means that in this case of very high concentration of I^- ion the excitation for the emission mentioned above does not take place on a singly localized I^- ion, but on an I^- ion which is arranged in such a way as a uniformly mixed KBr/KI crystal of 8.5×10^{-1} mol I^- ion concentration. In other words, the emission of localized type is yet originated from an I^- ion which is surrounded by many ions of the same kind in its neighbourhood in so large percentage as 85%. Nevertheless, the wave length of the emission does not approach that of the edge luminescence which should be found in a very pure KI crystal.

These facts are very interesting and we shall propose the following model for the exciton in KI. According to the usual theory of exciton, the migration of exciton is derived through the configurational interaction. In the present experiment, however, a small disturbance, such as admixture of 15% KBr will give rise to, at least, the situation favourable for the localized exciton. In other words, the admixture of KBr makes the migration of exciton difficult. Probably the existence of negative ions of another kind will make especially the dipole-dipole interaction energy to decrease, and lead to the not much small effective mass of the exciton in KI. This suggestion is consistent with the fact that the oscillator strength of the absorption of the exciton is as small as 0.1⁹⁾, since the smaller oscillator strength of the exciton absorption means the larger effective mass of the exciton⁹⁾.

The last question is that should the emission of the localized type at 305 m μ really

approach the edge luminescence in position? We were not able to find emissions peaking in the intermediate region between $305\text{ m}\mu$ and $220\text{ m}\mu$. If the exciton is in the electronic state in which it is able to emit its edge luminescence, it may migrate through the crystal and meet impurities or defects, emitting no edge luminescence. In the alloyed crystal of higher KI concentration, an I^- ion has many ions of the same kind as its neighbours, so the excitation energy at the ion may be transferred one by one, meeting the impurity at last and displaying the emission at $360\sim 380\text{ m}\mu$. Although the excited state around the I^- ion may change its electronic structure abruptly from the localized type to that of the migration type while the KI concentration becomes near the one of pure KI, the emission which should lie at the intermediate wave length region may be hardly caught experimentally. However, from the fact that only the emission at $305\text{ m}\mu$ and the one at $360\sim 380\text{ m}\mu$ both appears at the same time, the alternative assumption might be considered. The exciton in KI becomes self-trapped and displays the emission at $305\text{ m}\mu$ as intrinsic, and the energy of the trapped exciton is transferred by dipole-dipole interaction to the impurity, giving rise to the emission at $360\sim 380\text{ m}\mu$. It is necessary for this model to clarify the detailed properties of the unknown centers.

§ 5. Summary

In alloyed crystal of KBr/KI , a singly localized I^- ion and aggregated I^- ion emit

luminescences at $290\text{ m}\mu$ and $315\text{ m}\mu$ respectively which are suffered with Stokes shift. Both emissions coincide at $305\text{ m}\mu$ in cases of high concentrations of I^- ion. On the other hand an emission at $360\sim 380\text{ m}\mu$ which is found in pure KI appears in these cases. The latter emission is attributed to some unknown impurities to which the excitation energy at the I^- ion is transferred.

In view of the facts that the emission of localized type is yet observed even in the case of 8.5×10^{-1} mol KI concentration and the position of the emission does not approach to that of the edge luminescence, the nature of the exciton is discussed. The exciton in KI has a such electronic structure as the one which changes to a localized electronic structure with admixture of only 15% KBr .

We would like to thank Mr. S. Kitabayashi for his aid with the optical absorption measurement.

References

- 1) F. Seitz: *Rev. Mod. Phys.* **26** (1954) 29.
- 2) W. Van Sciver and R. Hofstadter: *Phys. Rev.* **97** (1955) 1181.
- 3) K. J. Teegarden: *Phys. Rev.* **105** (1957) 1222.
- 4) J. Frenkel: *Phys. Rev.* **37** (1931) 17.
- 5) M. Tomura: to be published afterwards.
- 6) W. R. Heller and A. Marcus: *Phys. Rev.* **84** (1951) 809.
- 7) S. Vavilov: *Doklady Akad. Nauk. S. S. S. R.* **67** (1949) 811.
- 8) M. Tomura: reported at the meeting of the Phys. Soc. Japan, Oct. 1958.
- 9) F. Seitz: *Rev. Mod. Phys.* **26** (1954) 28.

Flow of a Viscous, Electrically Conducting Fluid along a Circular Cylinder or a Flat Plate with Uniform Suction

By Michiru YASUHARA

*Department of Aeronautical Engineering, Nagoya University,
Nagoya, Japan*

(Received October 2, 1959)

An exact solution of the flow of a viscous, electrically conducting fluid with an externally imposed magnetic field normal to the wall is obtained for the incompressible flow along a circular cylinder or a flat plate with uniform suction. Analytical results show that if the Alfvén wave velocity is smaller than the suction velocity, a physically possible solution is obtained under a given boundary condition, and that the applied magnetic field acts on the flow as a decelerating action as expected from the general property of magnetic force, and as a result of this nature, the coefficient of skin-friction is reduced and that of Maxwell's stress is increased, while the total drag is kept unchanged. Further, the solution reduces to that of the asymptotic suction flow of a non-conducting fluid when the magnetic field tends to zero.

§ 1. Introduction

In recent years, effects of electro-magnetic field on the fluid flow have been investigated with increasing interests from the practical needs of the astronautics, plasma physics and the aero-space engineering. The fundamental equations controlling the continuum flow of a viscous, electrically conductive fluid have already been given, but as these equations are very complicated, only few analytical solutions were obtained for simplified cases.

The present paper gives another simplified solution for the suction flow. In the classical boundary layer theory, the aero-dynamic suction is used to prevent the flow separation, and except for high temperature fluids, such a method may also be applicable to the flow of electrically conductive fluids such as mercury etc.. The main influence of electro-magnetic field is caused by the interference between magnetic flux and fluid velocity, and from the general property of magnetic force, it can be estimated that the applied magnetic field acts on the flow as a decelerating action. The solution of the boundary layer over a circular cylinder with uniform suction were already given for non-conducting flow,¹⁾⁻³⁾ and above solutions will be extended to the case with externally imposed magnetic field normal to the wall surface.

§ 2. Fundamental Equations

The steady continuous flow of a viscous,

electrically neutral incompressible fluid is considered, and the rationalized m. k. s. system of electro-magnetic unit is used. The cylindrical case is chosen as a typical problem in the present paper, because the flat plate case can be obtained as the limiting case where the radius of cylinder becomes infinite.

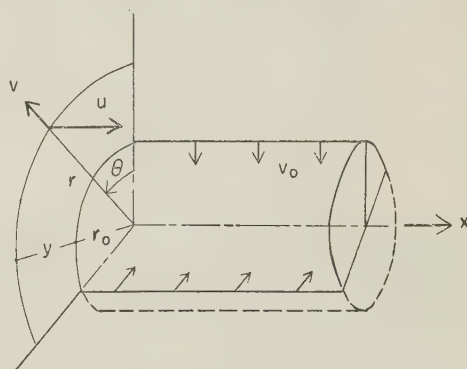


Fig. 1. Cylindrical co-ordinates.

If the cylindrical co-ordinates (x, r, θ) is chosen as shown in Fig. 1, and the asymptotic state in which all quantities are independent of x and θ is considered, then, terms operated by $\partial/\partial x$ and $\partial/\partial \theta$ should vanish. It is assumed that the θ -component of velocity and magnetic field do not appear in the flow field. Then, Maxwell's equations give

$$\nabla \times \mathbf{E} = 0: \quad dE_x/dr = 0, \quad (1)$$

$$(1/r)(d(rE_\theta)/dr) = 0, \quad (2)$$

$$\nabla \cdot \mathbf{E} = 0: (1/r)(d(rE_r)/dr) = 0, \quad (3)$$

$$\nabla \cdot \mathbf{B} = 0: (1/r)d(rB_r)/dr = 0, \quad (4)$$

$$\mathbf{j} = \sigma(\mathbf{E} + \mathbf{q} \times \mathbf{B}) = \frac{1}{\mu_e} \nabla \times \mathbf{B}:$$

$$j_z = \sigma E_z = 0, \quad (5)$$

$$j_r = \sigma(E_\theta - uB_\theta) = 0, \quad (6)$$

$$j_\theta = \sigma(E_r + uB_r - vB_x) = -\frac{1}{\mu_e} \cdot \frac{dB_x}{dr}, \quad (7)$$

where $\mathbf{E} = \mathbf{E}(E_z, E_r, E_\theta)$ represents the electric field intensity, $\mathbf{B} = \mathbf{B}(B_z, B_r, B_\theta)$ the magnetic flux density, $\mathbf{j} = \mathbf{j}(j_z, j_r, j_\theta)$ the electric current density, $\mathbf{q} = \mathbf{q}(u, v, 0)$ the velocity field, μ_e the magnetic permeability and σ the electrical conductivity. On the other hand, fluid dynamical equations give

$$\frac{1}{r} \frac{d(\rho vr)}{dr} = 0, \quad (8)$$

$$\rho v \frac{du}{dr} = \frac{1}{r} \frac{d}{dr} \left(\mu r \frac{du}{dr} \right) + j_r B_\theta - j_\theta B_r, \quad (9)$$

$$\rho v \frac{dv}{dr} = -\frac{dp}{dr} + \frac{4}{3} \mu \frac{d}{dr} \left\{ \frac{1}{r} \frac{d(vr)}{dr} \right\} + j_\theta B_x - j_x B_\theta, \quad (10)$$

where ρ represents the density, p the pressure and μ the coefficient of viscosity.

From Maxwell's equations, it is deduced that $\mathbf{E}$, $\mathbf{B}$ and $\mathbf{j}$ must be of the forms

$$\left. \begin{aligned} \mathbf{E} &= (E_z, E_r, E_\theta) = \left(0, 0, E_0 \frac{r_0}{r} \right), \\ \mathbf{B} &= (B_z, B_r, B_\theta) = \left(B_z, B_0 \frac{r_0}{r}, 0 \right), \\ \mathbf{j} &= (j_z, j_r, j_\theta) = \left(0, 0, -\frac{1}{\mu_e} \frac{dB_x}{dr} \right), \end{aligned} \right\} \quad (11)$$

to realize the possible solution of the present problem under initially given assumptions. In relations (11), r_0 represents the radius of cylinder and E_0 and B_0 are constant values of electric field intensity and magnetic flux density at the cylinder surface. Relations (11) represent that the electric field and the electric current have θ -component only, and further, E_θ and B_r must be proportional to $1/r$, respectively. In the limiting flat plate case where $r_0 \rightarrow \infty$, these correspond to constant values of E_0 and B_0 , respectively.

§ 3. Boundary Conditions

The boundary conditions on the velocity field are imposed by fluid mechanical considerations. If the flow is of the boundary layer type and externally imposed magnetic field is normal to the wall, these are

$$\left. \begin{aligned} u &\rightarrow u_\infty, \quad p \rightarrow p_\infty, \quad \text{and} \quad B_x \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty, \\ u &= 0, \quad \text{and} \quad v = v_0 \quad \text{at} \quad r = r_0, \end{aligned} \right\} \quad (12)$$

where v_0 represents the effective mean vertical velocity of fluid at the wall surface. While from electrodynamical considerations, the following relations must hold at the boundary between the fluid and solid wall.

$$\left. \begin{aligned} \{E_t\} &= 0, \\ \{H_t\} &= \mathbf{j}_s \times \mathbf{n}, \\ \{B_n\} &= 0, \end{aligned} \right\} \quad (13)$$

where the bracket represents the jump of values between quantities in the flow and the solid wall, $\mathbf{H}$ the magnetic field intensity which is equal to $\mathbf{B}/\mu_e$, suffix t and n the components tangential and normal to the wall surface respectively, $\mathbf{j}_s$ the surface current and $\mathbf{n}$ the unit vector normal to the surface. If the electrical conductivity of fluid and wall have finite values, there is no surface current and therefore $\mathbf{j}_s = 0$. In this case, above conditions reduce to:

$$E_{\theta 0} = E_{\theta w} = E_0, \quad (14)$$

$$\frac{B_{x0}}{\mu_e} = \frac{B_{xw}}{\mu_{ew}}, \quad (15)$$

$$B_{r0} = B_{rw} = B_0, \quad (16)$$

where suffices 0 and w represent values in fluid and in the wall next to the boundary surface, respectively.

Before proceeding to the flow solution, it is useful to study the electromagnetic field in the solid wall, to be continued with that in the flow. In the solid wall, it can be deduced that j_θ must vanish from Eqs. (9) and (11), as $u = 0$ there. Therefore Eq. (7) can be integrated to give

$$B_x = \text{const.} = B_{xw}, \quad (17)$$

and samely $E_\theta = vB_x$, which is reduced to

$$E_0 = v_0 B_{xw} \quad (18)$$

with the aid of Eqs. (11), (17) and (19). From above relations, it is known that the applied electric field E_θ induces the magnetic flux B_{xw} so as to cancel the electric current inside the wall.

§ 4. Incompressible Solution

In the present paper, calculations are accomplished for the most simple case in which the fluid is incompressible and all coefficients such as σ , μ_e , μ etc. are kept constant in the field. In this case, the equations can be in-

tegrated analytically and the typical effect of magnetic field on the suction characteristics is easily evaluated. Eq. (11) can be integrated to give

$$vr = v_0 r_0 = \text{const.} \quad (11)$$

Rewriting Eq. (9) with the aid of Eqs. (11) and (19), there is obtained

$$\rho v_0 r_0 \frac{du}{dr} = \frac{d}{dr} \left(\mu r \frac{du}{dr} \right) + \frac{B_0 r_0}{\mu_e} \frac{dB_x}{dr}. \quad (20)$$

Also from Eqs. (7), (11) and (19), the following relation is obtained

$$-\frac{1}{\mu_e} \frac{dB_x}{dr} = \frac{\sigma r_0}{r} (E_0 + u B_0 - v_0 B_x). \quad (21)$$

Applying the boundary condition (12) on Eq. (20), it is deduced that dB_x/dr must vanish as $r \rightarrow \infty$ because $du/dr \rightarrow 0$ there. Formally, this condition is automatically satisfied in Eq. (21) because the right-hand side tends to vanish at order $1/r$ as $r \rightarrow \infty$. However, this condition is not always satisfied, for, in the limiting flat plate case, r_0/r tends to unity and therefore the right-hand side does not always vanish except when the term in the brackets vanishes. Thus, the plausible condition compatible for both cases is given by

$$E_0 + u_\infty B_0 = 0. \quad (22)$$

The above relation gives the electric field intensity. Mathematically, the condition (22) makes the right-hand side of Eq. (21) to approach zero most steeply as r increases, which is similar to the method of steepest descent used in the classical boundary layer theory. From Eqs. (15), (18) and (22), the following relation is derived,

$$\frac{B_{xw}}{B_0} = \frac{1}{\varepsilon} \frac{B_{x0}}{B_0} = -\frac{u_\infty}{v_0}, \quad (23)$$

where

$$\varepsilon = \frac{\mu_e}{\mu_{ew}}. \quad (24)$$

Under these boundary conditions, the basic equations can be solved analytically as follows.

a) General case

First, two conditions are required to obtain a physically possible solution. These are

$$\left. \begin{aligned} v_0 < 0, \\ |v_0| > V_a \equiv B_0 / \sqrt{\rho \mu_e}, \end{aligned} \right\} \quad (25)$$

where V_a denotes the Alfvén wave velocity. In this case, the velocity, the magnetic flux and the pressure are given, respectively, by

$$1 - \frac{u}{u_\infty} = \left[\cosh \left(\frac{G}{2} \log Y \right) - \frac{S}{G} \sinh \left(\frac{G}{2} \log Y \right) \right] \times \exp \left(-\frac{R_e + R_m}{2} \log Y \right), \quad (26)$$

$$\frac{B_x}{B_0} = \frac{1}{G\alpha} \left[\{ 2R_m + (R_e - R_m)\varepsilon \} \sinh \left(\frac{G}{2} \log Y \right) + G\varepsilon \cosh \left(\frac{G}{2} \log Y \right) \right] \times \exp \left(-\frac{R_e + R_m}{2} \log Y \right), \quad (27)$$

$$\frac{p_\infty - p}{\rho u_\infty^2 / 2} = \frac{\alpha^2}{Y^2} + \frac{\alpha^2 H^2}{R_e R_m} \left(\frac{B_x}{B_0} \right)^2, \quad (28)$$

where

$$\left. \begin{aligned} R_e &= -\frac{\rho v_0 r_0}{\mu}, \quad R_m = -\sigma \mu_e v_0 r_0, \\ H &= \sqrt{\frac{\sigma}{\mu}} B_0 r_0, \quad G = \sqrt{(R_e - R_m)^2 + 4H^2}, \\ Y &= \frac{r}{r_0} = \frac{r_0 + y}{r_0}, \quad \alpha = -\frac{v_0}{u_\infty}, \\ S &= R_e - R_m - 2 \frac{H^2}{R_m} \varepsilon. \end{aligned} \right\} \quad (29)$$

H is the Hartmann number, R_e the Reynolds number and R_m the magnetic Reynolds number.

The coefficient of skin friction C_f and that of Maxwell's stress C_m are given, respectively, by

$$C_f = \frac{\mu(du/dr)_{r=r_0}}{\rho u_\infty^2 / 2} = 2\alpha \left\{ 1 - \left(\frac{V_a}{v_0} \right)^2 \varepsilon \right\}, \quad (30)$$

$$C_m = \frac{(B_0 B_x)_{r=r_0} / \mu_e}{\rho u_\infty^2 / 2} = 2\alpha \left(\frac{V_a}{v_0} \right)^2 \varepsilon. \quad (31)$$

Above relations show that C_f is decreased and C_m is increased as V_a increases, but the total drag $C_f + C_m$ is kept unchanged at a value of 2α , which is the same as in the non-magnetic flow.

b) $B_0 = 0$

When there is no magnetic field, $B_0 = 0$ and the solution becomes

$$\left. \begin{aligned} 1 - \frac{u}{u_\infty} &= \left(\frac{r_0 + y}{r_0} \right)^{\rho v_0 r_0 / \mu}, \\ \frac{B_x}{B_0} &= 0, \\ \frac{p_\infty - p}{\rho u_\infty^2 / 2} &= \frac{\alpha^2}{Y^2}. \end{aligned} \right\} \quad (32)$$

This solution coincides with Wüst⁽¹⁾, Lew⁽²⁾ and Yasuhara's⁽³⁾ solution for the asymptotic cylindrical suction flow of an incompressible fluid.

c) Two-dimensional case

In the limiting case when r_0 tends to infinity, the solution gives the two-dimensional one. In this case, E_θ represents the component normal to x and y directions, and B_r and v the y -component, and they have next forms,

$$\left. \begin{aligned} E_\theta &= E_0, \\ B_r &= B_0, \\ v &= v_0. \end{aligned} \right\} \quad (33)$$

If the limiting relation

$$\lim_{r_0 \rightarrow \infty} r_0 \log \frac{r_0 + y}{r_0} = y,$$

is applied on Eqs. (26), (27) and (28), these are reduced to

$$1 - \frac{u}{u_\infty} = \left[\cosh \left(\frac{G'}{2} Y' \right) - \frac{S'}{G'} \sinh \left(\frac{G'}{2} Y' \right) \right] \times \exp \left(- \frac{R_e' + R_m'}{2} Y' \right), \quad (34)$$

$$\frac{B_x}{B_0} = \frac{1}{G' \alpha} \left[\{ 2R_m' + (R_e' - R_m') \varepsilon \} \sinh \left(\frac{G'}{2} Y' \right) + G' \varepsilon \cosh \left(\frac{G'}{2} Y' \right) \right] \times \exp \left(- \frac{R_e' + R_m'}{2} Y' \right), \quad (35)$$

$$\frac{p_\infty - p}{\rho u_\infty^2 / 2} = \frac{\alpha^2 H'^2}{R_e' R_m'} \left(\frac{B_x}{B_0} \right)^2, \quad (36)$$

where

$$\left. \begin{aligned} R_e' &= - \frac{\rho v_0 L}{\mu}, \quad R_m' = - \sigma \mu_0 v_0 L, \\ H' &= \sqrt{\frac{\sigma}{\mu}} B_0 L, \quad G' = \sqrt{(R_e' - R_m')^2 + 4H'^2}, \\ Y' &= \frac{y}{L}, \quad S' = R_e' - R_m' - 2 \frac{H'^2}{R_m'} \varepsilon, \end{aligned} \right\} \quad (37)$$

and L is a reference length which, practically, has no influence on the solution. While C_f and C_m are kept unchanged, that is, given by relations (30) and (31), respectively. Further, if $B_0=0$, (34) becomes

$$1 - \frac{u}{u_\infty} = e^{-R_e' Y'} = e^{\rho v_0 y / \mu}, \quad (38)$$

which coincides with the asymptotic flat plate suction flow of an incompressible fluid.

§ 5. Calculations and Discussions

Velocity profiles calculated by the above results for cylindrical cases are shown in Fig. 2 for several values of H in the cases of R_e

$=100$, $R_m=1$ and of $R_e=10$, $R_m=10$. In both cases, the condition $|v_0| > V_a$ corresponds to

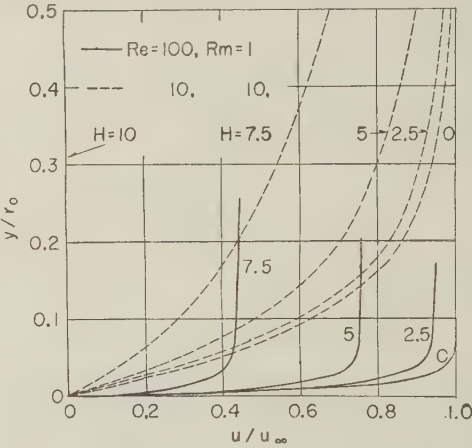


Fig. 2. Velocity profiles for a flat plate.

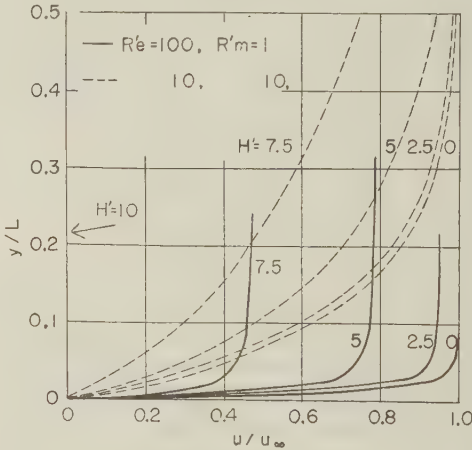


Fig. 3. Velocity profiles for a circular cylinder.

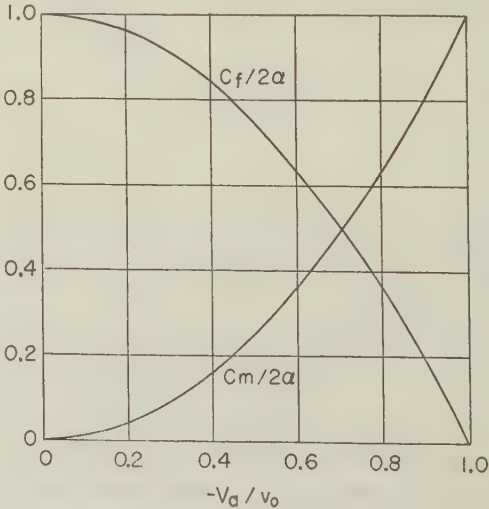


Fig. 4. Curves of coefficients as functions of $-V_a/v_0$, for $\varepsilon=1$.

$H < 10$. Similar results of the flat plate case are shown in Fig. 3 for several values of H' in cases of $R_e' = 100$, $R_m' = 1$ and of $R_e' = 10$, $R_m' = 10$. The condition $|v_0| > V_a$ also corresponds to $H' < 10$. $C_f/2\alpha$ and $C_m/2\alpha$ are shown in Fig. 4 as functions of $V_a/(-v_0)$.

From these figures, it is found that the applied magnetic flux B_r acts on the flow as a decelerating action. This is an expected property of the magnetic force. In the above calculations, the electric field E_θ is determined so that its coefficient E_0 should satisfy Eq. (22). The physical meaning of this is as follows. The above condition comes from the assumption that $u \rightarrow u_\infty$ as $r \rightarrow \infty$, and as a result of this condition, the induced electric current must vanish as $r \rightarrow \infty$, and in order to satisfy this condition, the electric field E_θ must be imposed on the flow so as to cancel the induced electric field. Practically, such a model is equivalent to the one in which the imposed magnetic flux B_r is moving in the x -direction with uniform velocity u_∞ . In this case, there is no interacting motion between the velocity field and the magnetic field in the flow field far distant from the wall.

§ 6. Conclusion

An exact solution of the flow of a viscous, electrically conducting fluid with an external-

ly imposed magnetic field normal to the wall is obtained for the incompressible flow over a circular cylinder or a flat plate with uniform suction. The solution is an extension of that of the classical boundary layer flow with uniform suction. Analytical results show that if the Alfvén wave velocity is smaller than the suction velocity, a physically possible solution is obtained under a given boundary condition. Numerical results show that the applied magnetic field acts on the flow as a decelerating action as expected from the general property of the magnetic force, and the coefficient of skin-friction is reduced and that of Maxwell's stress is increased, while the total drag is kept unchanged. Further, the solution reduces to that of the asymptotic suction flow when the imposed magnetic field tends to zero.

Present analysis may be extended to the compressible case if characteristics of the flow parameters are given.

Finally, present work was partially financed by the Scientific Research Fund by the Ministry of Education.

References

- 1) W. Wüst: *Ing. Arch.* **23** (1955) 198.
- 2) H. G. Lew: *J. Aero. Sci.* **23** (1956) 276.
- 3) M. Yasuhara: *Rep. Inst. Sci. Technol. Univ. Tokyo* **10** (1956) 131.

Two-dimensional Flow of an Ideal Gas with Small Electric Conductivity past a Thin Profile

By Takeo SAKURAI

*Department of Aeronautical Engineering, Faculty of Engineering,
Kyoto University*

(Received August 29, 1959)

Two dimensional flow of an ideal gas with small electric conductivity past a thin profile is investigated. The applied uniform magnetic field is assumed to make a small angle with the uniform flow at infinity. The usual thin wing expansion technique is applied and the linearized equation is derived. The linearized equation is solved for the case of flow past a symmetric profile using an approximate method similar to that of Oseen in the theory of viscous flow, and the first order effects of the conductivity and of the angle of inclination are examined. The subsonic as well as the supersonic flow cases are considered, and the lift and the drag due to the magnetic field are obtained. In the subsonic case, the lift vanishes while the drag is positive for any profile. In the supersonic case, the lift is found to be negatively proportional to the angle of inclination, while the drag is not affected by the presence of the magnetic field. An intuitive explanation of the results is also included.

§ 1. Introduction

Recently Resler and Sears²⁾ investigated the two-dimensional flow of an incompressible ideal fluid with electric conductivity past a two-dimensional thin profile. The applied uniform magnetic field is assumed to be parallel or perpendicular to the direction of the uniform flow at infinity. They considered the flow with infinite conductivity using the usual thin wing expansion technique, and obtained results which show the change of the lift and the appearance of the drag due to the magnetic field. They examined, further, the effect of large but finite electric conductivity using the boundary layer technique. According to a Sears' lecture*, Resler also investigated the flow of a compressible ideal gas with infinite electric conductivity past a thin profile, and obtained an interesting partial differential equation of the second order which changes its type depending on the Alfvén number as well as the Mach number of the uniform flow. Taniuchi and Kato³⁾ investigated systematically the characteristics of the basic equation for the two-dimensional flow of a compressible fluid with infinite electric conductivity and obtained results which may be

compared with that of Resler. He considered also the exact equation (not linearized) of the flow with the magnetic field applied parallel to the uniform flow and suggested that the usual hodograph method can be applied. Andō¹⁾ investigated basic equations of the problem for the case with finite electric conductivity and introduced the generalized velocity potential. He discussed the cases of infinite electric conductivity in detail, and considered the flow over a wavy wall when the applied magnetic field is inclined with respect to the uniform flow.

The investigation of the flow with infinite electric conductivity is very instructive, because it gives us insight into the more complicated phenomena with finite conductivity. The electric conductivity in the ionosphere, on the other hand, is considered to be very small. Hence, it seems to be of importance to examine the effect of the small electric conductivity. In the present paper, we deal with the two-dimensional flow of an ideal gas with small electric conductivity past a two-dimensional thin profile. The applied uniform magnetic field is assumed to make a small angle with the direction of the uniform flow at infinity. The usual thin wing expansion technique is applied and a linearized fundamental equation is obtained. The equation is solved for the case of flow past a symmetric

* given at the 8th Japan National Congress of Applied Mechanics held in Tokyo, in September, 1958.

profile using an approximate method similar to that of Oseen in the theory of viscous flow. Only the first order effect of the conductivity and of the angle of inclination is examined. The subsonic as well as the supersonic flow cases are considered, and the lift and the drag due to the magnetic field are obtained.

§ 2. Basic Equation

The basic equations of the steady flow of a compressible ideal gas with electric conductivity are in MKS system of units:

$$\text{rot } \mathbf{E} = 0, \quad \text{div } \mathbf{E} = 0, \quad (1)$$

$$\text{rot } \mathbf{B} = R_m \mathbf{J}, \quad \text{div } \mathbf{B} = 0, \quad (2)$$

$$\mathbf{J} = \mathbf{E} + \mathbf{u} \times \mathbf{B}, \quad (3)$$

$$\text{div } (\rho \mathbf{u}) = 0, \quad (4)$$

$$\left. \begin{aligned} \rho \frac{D\mathbf{u}}{Dt} &= -\text{grad } p + K(\mathbf{J} \times \mathbf{B}), \\ \frac{D}{Dt} &= (\mathbf{u} \cdot \text{grad}), \end{aligned} \right\} \quad (5)$$

$$\frac{\rho}{\gamma - 1} \frac{DT}{Dt} = -p \text{div } \mathbf{u} + KJ^2, \quad K = \frac{R_m}{M_A^2}, \quad (6)$$

$$p = \rho T, \quad (7)$$

where

$$\hat{\mathbf{r}} = \hat{L} \mathbf{x}, \quad (8)$$

$$\left. \begin{aligned} \hat{\mathbf{u}} &= \hat{u}_0 \mathbf{u}, \quad \hat{p} = \hat{\rho}_0 \hat{u}_0^2 p, \\ \hat{\rho} &= \hat{\rho}_0 \rho, \quad \hat{T} = \frac{\hat{u}_0^2}{R} T, \end{aligned} \right\} \quad (9)$$

$$\left. \begin{aligned} \hat{\mathbf{B}} &= \hat{B}_0 \mathbf{B}, \\ \hat{\mathbf{E}} &= \hat{u}_0 \hat{B}_0 \mathbf{E}, \\ \hat{\mathbf{J}} &= \sigma \hat{u}_0 \hat{B}_0 \mathbf{J}, \end{aligned} \right\} \quad (10)$$

$$R_m = \mu_e \sigma \hat{L} \hat{u}_0, \quad M_A^2 = \frac{\hat{\rho}_0 \hat{u}_0^2}{\hat{B}_0^2 / \mu_e}. \quad (11)$$

In these equations, $\hat{\mathbf{r}}$ is the Cartesian coordinates in which the direction of the $\hat{x}$ -axis coincides with that of the uniform flow at infinity, and $\hat{L}$ is the characteristic length of the problem, for example, the chord length of the profile. $\hat{\mathbf{u}}$, $\hat{p}$, $\hat{\rho}$, $\hat{T}$, $\hat{\mathbf{B}}$, $\hat{\mathbf{E}}$ and $\hat{\mathbf{J}}$ are the velocity, the density, the pressure, the temperature, the magnetic flux, the electric field and the current density respectively. γ , R , σ and μ_e are respectively the ratio of the specific heats, the universal gas constant, the electric conductivity and the permeability of the gas. The letters with circumflex $\wedge$ and with suffix $_0$ indicate respectively the quantity

with dimension and the quantity at infinity. The nondimensional parameters R_m and M_A are called in usual the magnetic Reynolds number and the Alfvén number.

From Eq. (1), we obtain

$$\mathbf{E} = \text{grad } \phi_B, \quad \Delta \phi_B = 0, \quad (12)$$

where ϕ_B is the electric potential. Then $\mathbf{E}$ is constant throughout the flow field provided that there is no electric pole, and the constant is determined from Eq. (3) and the boundary condition that the current must vanish at infinity, so that

$$\mathbf{E} = -\mathbf{i} \times \mathbf{B}_0, \quad (13)$$

where $\mathbf{i}$ is the unit vector in the direction of the x -axis.

If we assume

$$\mathbf{u} = (u, v, 0), \quad \mathbf{B} = (B_x, B_y, 0), \quad (14)$$

we obtain

$$\mathbf{J} = (0, 0, J), \quad \mathbf{E} = (0, 0, E), \quad (15)$$

from Eq. (2) and (13). Introducing these into Eqs. (1)–(7), we obtain the basic equations for the two-dimensional flow:

$$\frac{\partial B_y}{\partial x} - \frac{\partial B_x}{\partial y} = R_m J, \quad \frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} = 0, \quad (16)$$

$$J = E + (u B_y - v B_x), \quad E = -\sin \delta, \quad (17)$$

$$\frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial y} (\rho v) = 0, \quad (18)$$

$$\rho \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = -\frac{\partial p}{\partial x} - K B_y J, \quad (19)$$

$$\rho \left(u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial y} + K B_x J, \quad (20)$$

$$\frac{\rho}{\gamma - 1} \left(u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = -p \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + K J^2, \quad (21)$$

$$p = \rho T, \quad (22)$$

where δ is the angle between the applied uniform magnetic flux and the x -axis (Fig. 1).



Fig. 1.

In this paper, we consider a uniform flow past a thin profile. Then we may linearize the basic equations by making use of the usual thin wing expansion technique to obtain the following equations:

$$\frac{\partial B_y'}{\partial x} - \frac{\partial B_x'}{\partial y} = R_m J_1, \quad \frac{\partial B_x'}{\partial x} + \frac{\partial B_y'}{\partial y} = 0, \quad (23)$$

$$J_1 = B_y' + u_1 \sin \delta - v_1 \cos \delta, \quad (24)$$

$$\frac{\partial \rho_1}{\partial x} + \left(\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} \right) = 0, \quad (25)$$

$$\frac{\partial u_1}{\partial x} = -\frac{\partial p_1}{\partial x} - K J_1 \sin \delta, \quad (26)$$

$$\frac{\partial v_1}{\partial x} = -\frac{\partial p_1}{\partial y} + K J_1 \cos \delta, \quad (27)$$

$$\frac{1}{\gamma-1} \frac{\partial T_1}{\partial x} = -\dot{p}_0 \left(\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} \right), \quad (28)$$

$$p_1 = T_0 \rho_1 + T_1, \quad (29)$$

where

$$\left. \begin{aligned} u &= 1 + \varepsilon u_1, & v &= \varepsilon v_1, \\ \rho &= 1 + \varepsilon \rho_1, & p &= p_0 + \varepsilon p_1, & T &= T_0 + \varepsilon T_1, \end{aligned} \right\} \quad (30)$$

$$\left. \begin{aligned} B_x &= \cos \delta + \varepsilon B_x', & B_y &= \sin \delta + \varepsilon B_y', \\ J &= \varepsilon J_1. \end{aligned} \right\} \quad (31)$$

ε is a small parameter which expresses the order of the disturbances induced by the profile, and we have neglected the second order terms in ε to derive the above equations.

From Eqs. (25), (28), (29), we get

$$(\gamma-1)\rho_1 = \frac{T_1}{T_0}, \quad \rho_1 = M_0^2 p_1, \quad M_0^2 = \frac{u_0^2}{a_0^2}, \quad (32)$$

where a_0 is the speed of sound at infinity. Elimination of p_1 and ρ_1 from Eqs. (25), (26) and (32) yields the following equation

$$(1-M_0^2) \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} = K M_0^2 J_1 \sin \delta. \quad (33)$$

Eqs. (23), (24), (26), (27) and (33) are the basic equations for the present problem. Solution of these linearized equations is still very difficult for the general case, so that we shall restrict ourselves to the special case $R_m \ll 1$, $\delta \ll 1$ in the following.

§ 3. Flow with Slightly Inclined Magnetic Field

Eqs. (23)–(29) suggest that we may apply the small perturbation method with respect to R_m and expand all the quantities in powers of R_m . The zeroth approximation gives the usual Prandtl-Glauert flow and the undisturbed magnetic field. Then, inserting the results again into the basic equations and comparing the order of the first and the third term in

Eq. (26), we find that the third term becomes larger at great distances from the profile and hence straightforward application of the perturbation method will fail there. The situation is quite similar to that of Whitehead's paradox in the theory of viscous flow, which suggests the necessity of use of the method similar to that of Oseen.

If we neglect the terms involving R_m but retain those involving K in Eqs. (23)–(29), we obtain

$$\frac{\partial B_y'}{\partial x} - \frac{\partial B_x'}{\partial y} = 0, \quad \frac{\partial B_x'}{\partial x} + \frac{\partial B_y'}{\partial y} = 0, \quad (34)$$

$$J_1 = B_y' + u_1 \delta - v_1, \quad (35)$$

$$(1-M_0^2) \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} = K M_0^2 J_1 \delta, \quad (36)$$

$$\frac{\partial u_1}{\partial x} = -\frac{\partial p_1}{\partial x} - K \delta J_1, \quad (37)$$

$$\frac{\partial v_1}{\partial x} = -\frac{\partial p_1}{\partial y} + K J_1, \quad (38)$$

where we have made further approximation that $\delta \ll 1$ neglecting the terms of order δ^2 .

From Eq. (34), we can conclude that $\mathbf{B}' = 0$ by means of the discussion similar to that for $\mathbf{E}$. Then, the rest of the above equations constitutes the basic equations for the purely hydrodynamic variables. The difference of the above and the usual equations consists in the last terms of the Eqs. (36), (37) and (38) which represent the effect of the Lorentz force. If we eliminate J_1 and p_1 we obtain

$$\frac{\partial u}{\partial \xi} \pm \frac{\partial v}{\partial \eta} = \mp \frac{K M_0^2 \delta}{\sqrt{\pm(1-M_0^2)}} v, \quad (39)$$

$$\frac{\partial u}{\partial \eta} - \frac{\partial v}{\partial \xi} = K \left\{ v - \frac{(2-M_0^2)\delta}{\sqrt{\pm(1-M_0^2)}} u \right\}, \quad (40)$$

$$u_1 = u, \quad v_1 = v \sqrt{\pm(1-M_0^2)}, \quad (41)$$

$$\xi = x, \quad \eta = y \sqrt{\pm(1-M_0^2)}, \quad (42)$$

where the upper and the lower signs correspond to the subsonic and the supersonic flow, respectively.

The boundary conditions are the same as those of the usual thin wing theory

1) (u, v) is one-valued and continuous throughout the flow field,

2) $(u, v) \rightarrow 0$ as $|\xi|, |\eta| \rightarrow \infty$,

3) $v_1 = \pm f_B'(x)$ on $y=0$,

where the profile is expressed as $y = \pm t f_B(x)$.

1) *Subsonic flow*

From Eqs. (39) and (40), the velocity poten-

tial Φ as well as the stream function Ψ may be introduced:

$$\left. \begin{aligned} u &= \exp \left\{ -K\xi - \frac{K\delta(2-M_0^2)}{\sqrt{1-M_0^2}}\eta \right\} \frac{\partial \Phi}{\partial \xi}, \\ v &= \exp \left\{ -K\xi - \frac{K\delta(2-M_0^2)}{\sqrt{1-M_0^2}}\eta \right\} \frac{\partial \Phi}{\partial \eta}, \end{aligned} \right\} \quad (43)$$

$$\left. \begin{aligned} u &= \exp \left(-\frac{K\delta M_0^2 \eta}{\sqrt{1-M_0^2}} \right) \frac{\partial \Psi}{\partial \eta}, \\ v &= -\exp \left(-\frac{K\delta M_0^2 \eta}{\sqrt{1-M_0^2}} \right) \frac{\partial \Psi}{\partial \xi}, \end{aligned} \right\} \quad (44)$$

The fundamental solutions of the above equations are

$$\Phi_n = \exp \left\{ \frac{K\xi}{2} + K\delta\eta\sqrt{1-M_0^2} \right\} K_n \left(\frac{c}{2}r \right) e^{in\theta}, \quad (45)$$

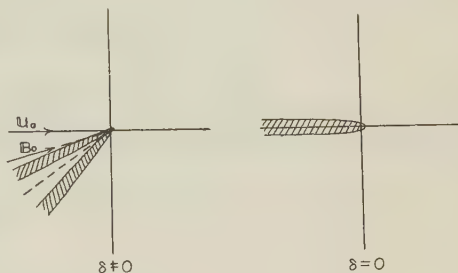
$$\Psi_n = \exp \left\{ -\frac{K\xi}{2} - K\delta\eta\sqrt{1-M_0^2} \right\} K_n \left(\frac{c}{2}r \right) e^{in\theta}, \quad (46)$$

$$\frac{c^2}{4} = \frac{K^2}{4} + K^2\delta^2(1-M_0^2), \quad (47)$$

where Φ_0 corresponds to a source and Ψ_0 to a vortex. From the asymptotic expansions of the above solutions we obtain

$$u, v \propto \exp \left\{ -\left(\frac{K\xi}{2} + \frac{K\delta\eta}{\sqrt{1-M_0^2}} + \frac{cr}{2} \right) \right\}. \quad (48)$$

The second term in the brackets suggests that the solutions diverge at infinity in the transonic case, and hence the following conclusions related to δ cannot be valid for the transonic flow. Further, the above equation shows the fact that a wake (or wakes) appears in the following direction (Fig. 2):



xy -plane

Fig. 2.

$$\theta = \pi + a\delta, \quad a = \frac{2}{\sqrt{1-M_0^2}} \{1 \pm M_0\sqrt{1-M_0^2}\}. \quad (49)$$

By analogy of the usual thin wing theory, the flow past a profile can be represented by suitable distribution of sources and vortices on the chord line of the profile:

$$u = u_1 + u_2, \quad v = v_1 + v_2, \quad (50)$$

$$\left. \begin{aligned} u_1 &= \exp \left\{ -K\xi - \frac{K\delta(2-M_0^2)}{\sqrt{1-M_0^2}}\eta \right\} \frac{\partial \Phi}{\partial \xi}, \\ v_1 &= \exp \left\{ -K\xi - \frac{K\delta(2-M_0^2)}{\sqrt{1-M_0^2}}\eta \right\} \frac{\partial \Phi}{\partial \eta}, \\ \Phi &= \int_{-1}^1 f(\xi_0) \exp \left(\frac{K(\xi - \xi_0)}{2} + K\delta\eta\sqrt{1-M_0^2} \right) K_0 \left(\frac{c}{2} \sqrt{(\xi - \xi_0)^2 + \eta^2} \right) d\xi_0, \end{aligned} \right\} \quad (51)$$

$$\left. \begin{aligned} u_2 &= \exp \left(-\frac{K\delta\eta M_0^2}{\sqrt{1-M_0^2}} \right) \frac{\partial \Psi}{\partial \eta}, \\ v_2 &= -\exp \left(-\frac{K\delta\eta M_0^2}{\sqrt{1-M_0^2}} \right) \frac{\partial \Psi}{\partial \xi}, \\ \Psi &= \int_{-1}^1 g(\xi_0) \exp \left\{ -\frac{K(\xi - \xi_0)}{2} - K\delta\eta\sqrt{1-M_0^2} \right\} K_0 \left(\frac{c}{2} \sqrt{(\xi - \xi_0)^2 + \eta^2} \right) d\xi_0. \end{aligned} \right\} \quad (52)$$

In the above, the first term (u_1, v_1) represents mainly the disturbance due to the symmetric profile immersed in the flow with applied field parallel to the direction of the uniform flow at infinity. The second term represents, on the other hand, the effect of the inclined magnetic field. Because of our assumption $K \ll 1$ and $\delta \ll 1$, we can expand the integrands of Eqs. (51) and (52) in the neighbourhood of the profile:

$$\begin{aligned} v &= \exp(-K\xi) \left[\mp \pi f(\xi) - K\delta\sqrt{1-M_0^2} \left\{ F(\xi_0) \log |\xi - \xi_0| \right\}_{-1}^1 \right. \\ &\quad \left. + C \int_{-1}^1 \frac{F(\xi_0)}{\xi - \xi_0} d\xi_0 \right] - C \int_{-1}^1 \frac{g(\xi_0)}{\xi - \xi_0} d\xi_0, \end{aligned} \quad (53)$$

$$F(\xi_0) = \int_{-1}^{\xi_0} f(\tau) d\tau, \quad (54)$$

where only the principal terms are retained. If we insert these into the boundary condition 3), and solve iteratively, we obtain

$$f(\xi) = -\frac{f_B'(\xi) \exp(K\xi)}{\pi\sqrt{1-M_0^2}}, \quad (55)$$

$$g(\xi) = -\frac{K\delta f_B(\xi)}{\pi} + O(K^2\delta). \quad (56)$$

Introducing the solutions (55) and (56) into Eqs. (51) and (52) we can calculate the velocity at any point in the flow field, and especially the velocity distribution over the profile:

$$u = (\pi\sqrt{1-M_0^2})^{-1} C \cdot \int_{-1}^1 \frac{f_B'(\xi_0)}{\xi - \xi_0} d\xi_0 + \frac{K}{2\pi\sqrt{1-M_0^2}} \int_{-1}^1 f_B'(\xi_0) \log |\xi - \xi_0| d\xi_0 + \dots \\ \pm K\delta f_B(\xi) + \dots \quad (57)$$

The first term of the above equation is nothing but the usual Prandtl-Glauert solution, while the second and the third terms represent respectively the effect of the magnetic field applied parallel to the uniform flow and the effect of the inclined magnetic field.

The lift and the drag coefficients are defined as follows

$$C_D = \int_{-L}^L \hat{p} d\hat{y} / (\hat{\rho}_0 \hat{u}_0^2 L / 2) = 2t^2 \int_{-1}^1 p_1 f_B' d\xi_0, \quad (58)$$

$$C_L = \int_{-L}^L (\hat{p}_- - \hat{p}_+) d\hat{x} / (\hat{\rho}_0 \hat{u}_0^2 L / 2) = 2t \int_{-1}^1 (p_{1-} - p_{1+}) d\xi_0, \quad (59)$$

where p_1 is obtained by integrating Eq. (37) over the profile:

$$p_1 = -u_1 \pm K\delta f_B(\xi). \quad (60)$$

Introducing the above results into Eqs. (58), (59) and (60), we obtain

$$C_L = 0, \quad (61)$$

$$C_D = -\frac{Kt^2}{\pi\sqrt{1-M_0^2}} \int_{-1}^1 f_B' \left\{ \int_{-1}^1 f_B'(\xi_0) \log |\xi - \xi_0| d\xi_0 \right\} d\xi. \quad (62)$$

The integral in the above expression can be rewritten by integrating by parts and exchanging the order of integration in the form:

$$I = \int_{-1}^1 f_B'(\xi) \left\{ \int_{-1}^1 f_B'(\xi_0) \log |\xi - \xi_0| d\xi_0 \right\} d\xi \\ = \int_{-1}^1 f_B(\xi_0) \left\{ \int_{-1}^1 \frac{f_B'(\xi)}{\xi - \xi_0} d\xi \right\} d\xi_0.$$

The comparison of the integral in the brackets with the first term of Eq. (57) suggests that the integral may be regarded as the velocity distribution over the thin profile which is represented by $\eta = t f_B(\xi)$ in the (ξ, η) -plane. Thus the above can be rewritten as

$$I = -\frac{\pi}{t^2} \int_{-1}^1 \eta \left(\frac{\partial \tilde{\Phi}}{\partial \xi} - 1 \right) d\xi \\ = -\frac{\pi}{t^2} \int_{-1}^1 \eta (d\tilde{\Phi} - d\xi),$$

where $\tilde{\Phi}$ is the velocity potential of the problem and the terms of order t^3 in the integrand were neglected. Further let us suppose that the domain outside the profile in the (ξ, η) -plane is mapped conformally onto the domain outside the unit circle in the Z -plane by the following analytic function

$$\zeta = \xi + i\eta = \frac{1}{2} \left(Z + \frac{1}{Z} \right) + i \left(a_{-1}Z + a_0 + \sum_1^{\infty} a_n Z^{-n} \right), \quad (63)$$

where all the coefficients a_i are real by symmetry. Then, by means of the technique of the complex variables, the integral I can also be written in the following form:

$$\begin{aligned} I &= -\frac{\pi}{4it^2} \int_{-1}^1 \{ \zeta(Z) + \bar{\zeta}(\bar{Z}) \} \cdot \{ dF(Z) + d\bar{F}(\bar{Z}) - d\zeta(Z) - d\bar{\zeta}(\bar{Z}) \} \\ &= -\frac{\pi^2}{2} \left\{ (a_{-1} - a_1)^2 + \sum_2^{\infty} n a_n^2 \right\}, \end{aligned} \quad (64)$$

where F is the complex velocity potential.

2) Supersonic flow

From Eqs. (39) and (40), the velocity potential Φ is introduced:

$$\left. \begin{aligned} u &= \exp \left\{ -K\xi + \frac{K\delta\eta(M_0^2 - 2)}{\sqrt{M_0^2 - 1}} \right\} \frac{\partial \Phi}{\partial \xi}, \\ v &= \exp \left\{ -K\xi + \frac{K\delta\eta(M_0^2 - 2)}{\sqrt{M_0^2 - 1}} \right\} \frac{\partial \Phi}{\partial \eta}, \end{aligned} \right\} \quad (65)$$

$$\left. \begin{aligned} \Phi &= \exp \left\{ \frac{K\xi}{2} - K\delta_0\eta\sqrt{M_0^2 - 1} \right\} \phi, \\ \phi_{\xi\xi} - \phi_{\eta\eta} - \frac{L^2}{4}\phi &= 0, \quad \frac{L^2}{4} = \frac{K^2}{4} - K^2\delta_0^2(M_0^2 - 1). \end{aligned} \right\} \quad (66)$$

Eq. (66) is the familiar equation of telegraphy, which tells us that the disturbance cannot propagate in front of the Mach wave as in the usual supersonic flow. On the other hand, the disturbances damp as they travel along the Mach wave, due to the resistivity of the magnetic lines of force against the transverse motion.

By Riemann's method of integration, the flow past a profile can be solved in the following manner:

$$\phi_P = \frac{(\phi V)_A + (\phi V)_B}{2} - 2^{-1} \int_B^A \{ (V\phi_\mu - \phi V_\mu)\nu_n + (V\phi_\nu - \phi V_\nu)\mu_n \} ds, \quad (67)$$

$$\mu = \xi + \eta, \quad \nu = \xi - \eta, \quad (68)$$

where (ν_n, μ_n) are the direction cosines of the inward normal, the line integral is taken along ACB (Fig. 3), and V is the Riemann function which satisfies the following conditions:

- 4) $\frac{\partial^2 V}{\partial \mu \partial \nu} - \frac{L^2}{16} V = 0$,
- 5) $V_\nu = 0$ on AP ($\mu = \mu_P$),
 $V_\mu = 0$ on BP ($\nu = \nu_P$),
- 6) $V_P = 1$.

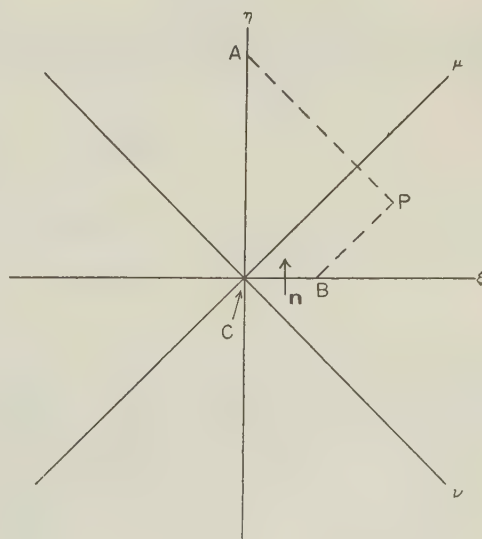


Fig. 3.

As mentioned above, the disturbances from the profile cannot propagate in front of the

Mach wave emanated from the leading edge of the profile, so that we may assume $\phi = \phi_\mu = \phi_\nu = 0$ on AC . Then, Eq. (67) can be simplified as follows:

$$\begin{aligned} \phi_P - \frac{\phi_B}{2} = & -\frac{1}{2\sqrt{2}} \int_{-1}^{\xi_P - \eta_P} \frac{\partial \phi}{\partial \eta} \bigg|_{\eta=0} I_1 \left(\frac{L}{2} \sqrt{(\xi_P - \xi)^2 - \eta_P^2} \right) d\xi \\ & + \frac{L}{4\sqrt{2}} \int_{-1}^{\xi_P - \eta_P} \phi \bigg|_{\eta=0} \frac{\eta}{\sqrt{(\xi_P - \xi)^2 - \eta_P^2}} I_1 \left(\frac{L}{2} \sqrt{(\xi_P - \xi)^2 - \eta_P^2} \right) d\xi, \end{aligned} \quad (69)$$

where the fact that $\nu_n = -\frac{1}{\sqrt{2}}$, $\mu_n = \frac{1}{\sqrt{2}}$ on $\overline{ABC}$, and

$$V = I_0 \left(\frac{L}{2} \sqrt{(\mu_P - \mu)(\nu_P - \nu)} \right), \quad (70)$$

has been taken into account. Thus, putting $\eta=0$ in (69), the velocity potential ϕ on the profile is obtained:

$$\phi_P \bigg|_{\eta=0} = -\frac{1}{\sqrt{2}} \int_{-1}^{\xi_P} \frac{\partial \phi}{\partial \eta} \bigg|_{\eta=0} I_0 \left(\frac{L(\xi_P - \xi)}{2} \right) d\xi. \quad (71)$$

Now, if we introduce Eq. (65) into the boundary condition 3), we have

$$\frac{f_B'(\xi)}{\sqrt{M_0^2 - 1}} = e^{-(K\xi/2)} \{ \phi_\eta - K\delta\sqrt{M_0^2 - 1} \phi \}. \quad (72)$$

Solving Eqs. (71) and (72) iteratively, we obtain

$$\phi = \phi_0 + K\delta\sqrt{M_0^2 - 1} \phi_1 + \dots, \quad (73)$$

$$\left. \begin{aligned} \phi_0 = & -\frac{1}{\sqrt{2(M_0^2 - 1)}} \int_{-1}^{\xi_P} e^{K\xi/2} f_B'(\xi) I_0 \left(\frac{L(\xi_P - \xi)}{2} \right) d\xi, \\ \phi_1 = & -\frac{1}{\sqrt{2}} \int_{-1}^{\xi_P} \phi_0 I_0 \left(\frac{L(\xi_P - \xi)}{2} \right) d\xi. \end{aligned} \right\} \quad (74)$$

From the above obtained solution, we can easily calculate the velocity distribution over the profile as well as the drag and the lift coefficients:

$$u = -\frac{f_B'(\xi)}{\sqrt{2(M_0^2 - 1)}} - \frac{K f_B(\xi)}{2\sqrt{2(M_0^2 - 1)}} \pm \frac{K\delta f_B(\xi)}{2}, \quad (75)$$

$$\left. \begin{aligned} C_D = & \frac{2t^2}{\sqrt{2(M_0^2 - 1)}} \int_{-1}^1 (f_B')^2 d\xi, \\ C_L = & -tK\delta \int_{-1}^1 f_B d\xi. \end{aligned} \right\} \quad (76)$$

In Eq. (79), the first term is the usual Prandtl-Glauert solution, the second term represents the effect of the magnetic field applied parallel to the direction of the uniform flow, and the third term corresponds to the effect of the inclined magnetic field. The double signs of the third term correspond to the upper and the lower side of the profile as is obvious from the consideration of symmetry.

§ 4. Concluding Remarks

Inspecting Eqs. (61), (62), (64) and (76), we can conclude that: in the subsonic flow, the lift vanishes and the drag is positive for any profile, while in the supersonic flow, the lift is negatively proportional to the angle of inclination of the magnetic field and no increase of the drag due to the magnetic field results. It is also to be noted that the results

concerning the lift are independent of the Mach number for both flows. The negative proportionality of the lift to the magnetic angle of inclination in the supersonic case may be explained intuitively by the resistivity of the magnetic lines of force against the transverse motion, the effect of which is, however, in the subsonic case, just cancelled out by the hydrodynamic force. The appearance of the drag in the subsonic case may also be ascribed to the same reason. As mentioned already, these conclusions cannot be applied to the case of the transonic flow. The fact that the increment of the drag just vanishes in the supersonic case will also be

restricted to the first order effect of K .

Acknowledgement

The author wishes to express his cordial thanks to Professor Ko Tamada for his continual and hearty guidance and encouragement.

References

- 1) S. Andō: to be published in this Journal.
- 2) E. L. Resler and W. R. Sears: *J. Fluid Mech.* **5** (1959) 257.
- 3) T. Taniuchi and Y. Kato: *Prog. Theor. Phys.* **21** (1959) 606.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

A New Type of Thermal Conductivity Gas Detector, I.

By Shinzan SÔMA and Yû TAKEUCHI

Faculty of Liberal Arts, Ibaraki University

(Received March 27, 1959)

A new type of gas detector with two thermistors and two thermister-cells was designed. Two thermistors were enclosed in each thermister-cells respectively, one of the cells having a porous window through which gases may run into the cell from the outside. Measuring the thermal conductivity of gas permeating into the cell through the porous window, we can detect the gas with high sensitivity. Since the cell is small, the time response is quick, and the sensitivity is increased because of the self-heating effect of the thermister. Using this method, we have been able to detect 0.01% hydrogen contained in air.

§ 1. Introduction

Although thermal conductivity apparatuses¹⁾ are widely used as gas analysers, they have the disadvantages that, in order to obtain high sensitivity with these apparatuses, gas-sampling bulb must be used and that long time is required to measure the thermal conductivity.

The authors designed a new apparatus characterised by high sensitivity, quick response and simplicity of measurement. As shown in Fig. 1, a bead-thermister a (or b) was enclosed in a small cell α (or β) on the inner wall of the tube with a diaphragm A (or B).

The diaphragm A is made of paper which is permeable to gases, while the other diaphragm

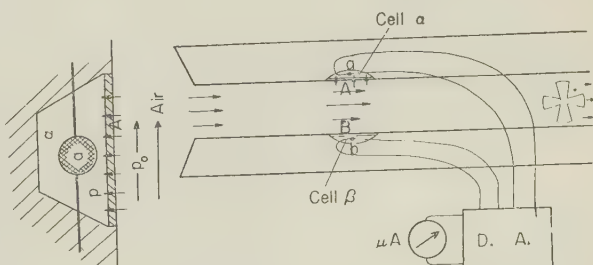


Fig. 1. Schematic arrangement of the apparatus.
 α, β thermister-cell; A, B diaphragms;
 a, b thermister.

B is impermeable to gases. Both thermistors a and b are heated by currents about 2 mA and the temperature difference between the thermistors a and b is measured by a differential amplifier. When the air current containing any impurity flows through the tube, the air in the cell α is replaced by the gas permeating through the diaphragm A , but the air in the cell β is not replaced. Since the temperature of the thermistor a changes with the variation of thermal conductivity of the gas in the cell α , the output signal of the differential amplifier depends on the impurity gas density in the cell α . The output signal is independent of the flow rate of the air in the tube, since the thermistor, the temperature sensing element, is enclosed in the cell and the air in the cell is almost at rest. The effect of the temperature of the air is cancelled, for the temperature variations of both thermistors occur simultaneously.

§ 2. Theory

Supposing that the air contains hydrogen, let the volume density of hydrogen in the air be p_0 , and the density in the cell be p (cf. Fig. 2). The quantity of the hydrogen permeating through the diaphragm A will be proportional to the difference of density $p_0 - p$.

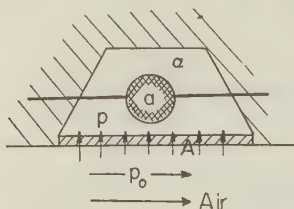


Fig. 2. α , Thermistor-cell; A diaphragm; a thermistor.

Therefore, we have

$$\frac{d(pV)}{dt} = kS(p_0 - p), \quad (1)$$

where V is the volume of cell, S the area of diaphragm and k the permeating velocity. Integrating (1) under the initial condition

$p=0$ for $t=0$, we obtain

$$p = p_0 \left\{ 1 - \exp\left(-\frac{kS}{V}t\right) \right\}. \quad (2)$$

In our arrangement $V \sim 1.5 \times 10^{-2} \text{ cm}^3$, $S \sim 1.2 \times 10^{-1} \text{ cm}^2$ and $k \sim 0.20 \text{ cm/sec}$, and we obtain $p = p_0/2$ at $t = 0.4 \text{ sec}$. Therefore the density p will become equal to p_0 almost instantly.

Next, we shall make an approximate evaluation of the temperature variation of the thermistor. Let T and T_0 denote the temperatures of the thermistor when the enclosed air has thermal conductivity k and k_0 respectively. Let R and Q denote the electric resistance and the Joules's heat respectively and R and Q be their values at $t=0$. Put

$$T = T_0 + \Delta T, \quad Q = Q_0 + \Delta Q, \quad R = R_0 + \Delta R. \quad (3)$$

From the temperature characteristics of the thermistor²⁾, we have

$$\log R = \frac{f}{T + 273} + \text{const},$$

where f is a characteristic constant. Therefore, we have

$$\frac{\Delta R}{R_0} = -\frac{f}{(T_0 + 273)^2} \Delta T. \quad (4)$$

Let the heat capacity of the thermistor be C , then we have

$$\frac{d(CT)}{dt} = Q - kg(T - \theta), \quad (5)$$

where kg is the coefficient of heat transfer from the thermistor to the surrounding medium and θ is the temperature of external air. At $t=0$, we have

$$Q_0 - k_0g(T_0 - \theta) = 0. \quad (6)$$

From (3) (5) and (6), we have

$$C \frac{d\Delta T}{dt} = \Delta Q + Q_0 \left(1 - \frac{k}{k_0} \right) - kg\Delta T. \quad (7)$$

Since in this apparatus the voltage between the terminals of the thermistor is kept nearly constant, we obtain

$$\Delta Q = -Q_0 \frac{\Delta R}{R_0}. \quad (8)$$

Then, from (4), (7) and (8), we have

$$C \frac{d\Delta T}{dt} = Q_0 \left(1 - \frac{k}{k_0} \right) + \left\{ \frac{Q_0 f}{(T_0 + 273)^2} - kg \right\} \Delta T. \quad (9)$$

Hence

$$\Delta T = -\frac{\left(\frac{k}{k_0} - 1 \right)}{\left\{ \frac{1}{T_0 - \theta} \frac{k}{k_0} - \frac{f}{(T_0 + 273)^2} \right\}} \left[1 - \exp \frac{1}{C} \frac{T_0 - \theta}{T_0 - \theta} \frac{k}{k_0} - \frac{f}{(T_0 + 273)^2} \right] Q_0 t. \quad (10)$$

In our apparatus $f=3.7\times10^3$ deg, $C=2\times10^{-5}$ cal/deg, $R=3.7\text{ k}\Omega$ and $Q_0=1.0\times10^{-2}$ watt at $\theta=18^\circ\text{C}$, so that $T=39^\circ\text{C}$. Substituting these values into (10), we have

$$\Delta T = -\frac{\frac{k}{k_0}-1}{0.048\left(\frac{k}{k_0}\right)-0.038}\left[1-e^{-\left(5.7\frac{k}{k_0}-4.5\right)t}\right].$$

(11)

According to (11), the time lag will become smaller as k/k_0 becomes larger, but even when k/k_0 is nearly equal to unity, the term containing t in (11) is given by $\exp(-1.2t)$, so that the thermister will reach the thermal

equilibrium rather rapidly. Therefore this method is suitable for quick measurements of thermal conductivity. The smallness of the denominator of (11) results in increased sensitivity of this apparatus.

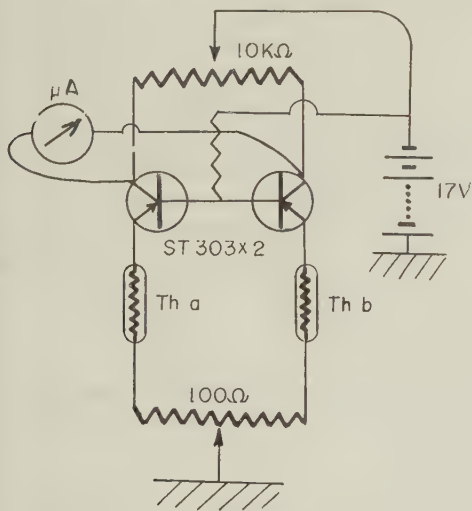


Fig. 3. Differential amplifier.

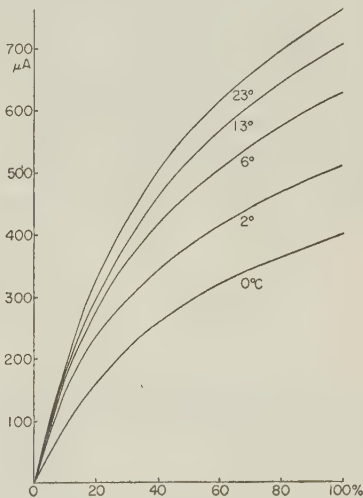


Fig. 5 (a). Out-put signal *vers.* density curve for various temperatures.

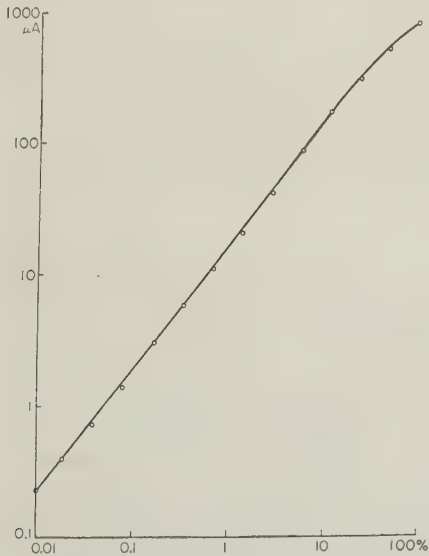


Fig. 4. Out-put signal *vers.* hydrogen density. Logarithmic scale.

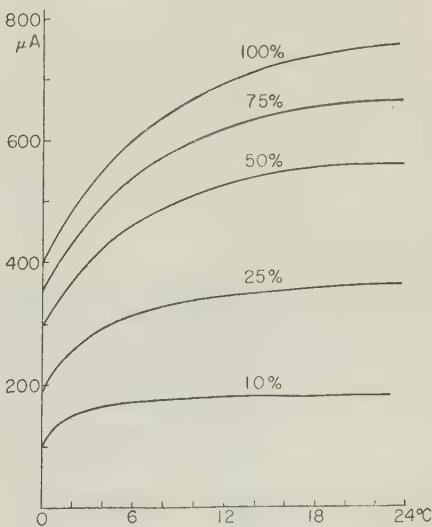


Fig. 5 (b). Temperature dependence of the output signal for various hydrogen densities.

§ 3. Experimental Results

A differential amplifier as shown in Fig. 3 was used. Fig. 4 shows the relation between the output signal and the hydrogen density when the temperature of external air is 20°C. The level of noise was less than 0.1 μ A. The sensitivity varies with the temperature of external air as shown in Fig. 5.

§ 4. Conclusion

Our present apparatus has following advantages:

- 1) The response is sufficiently rapid for use as a continuous gas detector.
- 2) The sensitivity is rather high in spite of the simplicity of apparatus. Craft paper is used in the present apparatus for the diaphragm A attached to thermister cell α . We are now in search of more suitable materials for the diaphragm in order to

increase the stability and durability of the detector and we shall report the details in a future publication.

The authors wish to express their hearty thanks to prof. J. Ôishi of Tokyo Institute of Technology for his kind advice and valuable discussion. Thanks are also due to prof. T. Awano of Ibaraki University for his support and encouragement and to prof. E. Takeda of Ibaraki University for his interest and kind inspection of the manuscript.

References

- 1) Kittaka et al: J. Appl. Phys. Japan **22** (1953) 119.
J. B. H. Kuper: Rev. Sci. Instrum. **8** (1937) 131.
C. C. Minter: Rev. Sci. Instrum. **29** (1958) 793.
R. H. Munch: Industr. Engng Chem. **37** (1945) 85.
- 2) J. A. Becker et al: Amer. Inst. Elect. Engr. **65** (1946) 771.
B. G. Gutmann et al: J. Appl. Phys. **21** (1950) 1267.

Non-ideality Effects upon the Sedimentation Equilibrium in a Density Gradient*

By Hiroshi FUJITA

*Physical Chemistry Laboratory, Department of Fisheries,
University of Kyoto, Maizuru*

(Received October 8, 1959)

The theory of Meselson *et al.* for the sedimentation equilibrium of a macromolecular solute in a density gradient of a low-molecular-weight substance is corrected for the thermodynamic non-ideality of the system. It is shown that equilibrium experiment of this type allows determination of the molecular weight of the macromolecular component if the "solvation" parameter at the limit of zero concentration of the macromolecule is constant throughout the cell.

§ 1. Introduction

Meselson, Stahl, and Vinograd¹⁾ have recently described an interesting type of sedimentation equilibrium experiment for a three-component system. The system contains, in addition to a solvent (component 0), a dilute macromolecular solute (component 1) and a moderately concentrated low-molecular-weight substance of high density (component 2). The

density of the latter component should be such that when the system is at sedimentation equilibrium the term $1 - \bar{v}_1 \rho$ for the macromolecular component vanishes at some point in the ultracentrifuge cell, where $\bar{v}_1$ is the partial specific volume of component 1 in the solution and ρ is the density of the solution. To treat this type of equilibrium experiment Meselson *et al.* assumed that the activity coefficient, γ_1 , of component 1 on the molality scale is unity for all concentrations of components 1 and 2. The purpose of the

* This investigation was supported by a grant from the National Science Foundation (G-3599).

present paper is to formulate a theory of this type of experiment without this assumption. In other words, we shall be interested in taking the thermodynamic non-ideality of the macromolecular component into theoretical consideration.

§ 2. Theory

The equations descriptive of the sedimentation equilibrium of a three-non-electrolyte component system are²⁾

$$M_1(1-\bar{v}_1\rho)\omega^2r = \left(\frac{\partial\mu_1}{\partial m_1}\right)_{P,m_2} \frac{dm_1}{dr} + \left(\frac{\partial\mu_2}{\partial m_1}\right)_{P,m_2} \frac{dm_2}{dr} \quad (1)$$

$$M_2(1-\bar{v}_2\rho)\omega^2r = \left(\frac{\partial\mu_2}{\partial m_1}\right)_{P,m_2} \frac{dm_1}{dr} + \left(\frac{\partial\mu_2}{\partial m_2}\right)_{P,m_1} \frac{dm_2}{dr} \quad (2)$$

where m_i is the concentration on the molality scale, μ_i is the chemical potential *per mole*, M_i is the molecular weight, and $\bar{v}_i$ is the partial specific volume, of component i ($i=1, 2$), ρ is the density of the solution, r is the radial distance from the axis of the rotor of the ultracentrifuge, ω is the rotor speed, and P is the pressure. Meselson *et al.* dealt with a macromolecular electrolyte in the presence of a low-molecular-weight 1-1 electrolyte, but the development here assumes, for simplicity of treatment, that all components are non-electrolytes. We further assume that the partial specific volumes of all components are constant.

If use is made of the "solvation" parameter Γ defined by

$$\Gamma = -\frac{(\partial\mu_2/\partial m_1)_{P,m_2}}{(\partial\mu_2/\partial m_2)_{P,m_1}} \quad (3)$$

Eqs. (1) and (2) may be rewritten

$$A_1 m_1 r = (1+m_1\beta_{11}) \frac{dm_1}{dr} - \Gamma(1+m_2\beta_{22}) \left(\frac{m_1}{m_2}\right) \frac{dm_2}{dr} \quad (4)$$

$$A_2 m_2 r = -\Gamma(1+m_2\beta_{22}) \frac{dm_1}{dr} + (1+m_2\beta_{22}) \frac{dm_2}{dr} \quad (5)$$

where A_i ($i=1, 2$) is

$$A_i = M_i(1-\bar{v}_i\rho)\omega^2/(RT) \quad (6)$$

and β_{11} and β_{22} are

$$\beta_{11} = (\partial \ln \gamma_1 / \partial m_1)_{P,m_2} \quad (7)$$

$$\beta_{22} = (\partial \ln \gamma_2 / \partial m_2)_{P,m_1} \quad (8)$$

The γ_i ($i=1, 2$) is the activity coefficient of component i on the molality scale and is

chosen so that it approaches unity as the concentrations of components 1 and 2 tend to zero.

If the solution is sufficiently dilute in component 1 but not so in component 2 Eqs. (4) and (5) may be replaced by

$$(A_1)_0 m_1 r = \frac{dm_1}{dr} - \Gamma_0 [1+m_2(\beta_{22})_0] \left(\frac{m_1}{m_2}\right) \frac{dm_2}{dr} \quad (9)$$

$$(A_2)_0 m_2 r = [1+m_2(\beta_{22})_0] \frac{dm_2}{dr} \quad (10)$$

where the subscript 0 indicates the value at the limit of zero concentration of component 1. Equations (9) and (10) have been derived by neglecting in Eqs. (4) and (5) the terms of order m_1 in comparison with unity or with the terms of order m_2 . Combining Eqs. (9) and (10) and rearranging yields

$$dm_1/dr = [(A_1)_0 + \Gamma_0(A_2)_0] m_1 r \quad (11)$$

Substitution for A_i from Eq. (6) and use of the assumption that $\bar{v}_i$ is constant leads to

$$\begin{aligned} \frac{dm_1}{dr} &= \left(\frac{\omega^2}{RT}\right) \{M_1[1-\bar{v}_1(\rho)_0] + \Gamma_0 M_2[1-\bar{v}_2(\rho)_0]\} m_1 r \\ & \quad (12) \end{aligned}$$

The quantity $(\rho)_0$, which may be a function of r , is obtained from the blank experiment in which only components 0 and 2 are present in the same amounts as in the solution experiment. We denote $(\rho)_0$ *vs.* r curve so obtained by $\rho_b(r)$. The quantity Γ_0 may also be a function of r and is appropriate to write $\Gamma_0(r)$. Then integration of Eq. (12) gives

$$\begin{aligned} &\ln [m_1(r)/m_1(r_0)] \\ &= (\omega^2/RT) \int_{r_0}^r \{M_1[1-\bar{v}_1(\rho)_0] + \Gamma_0 M_2[1-\bar{v}_2(\rho)_0]\} r dr \quad (13) \end{aligned}$$

where r_0 is some value of r to be determined below.

From Eq. (12) it follows that if conditions are chosen so that the quantity in the braces vanishes at a point in the cell the curve for m_1 *vs.* r has a maximum at that point. We choose this point as r_0 , and expand $\rho_b(r)$ and $\Gamma_0(r)$ in Taylor series about $r=r_0$. Then

$$\rho_b(r) = \rho_b(r_0) + \left(\frac{d\rho_b}{dr}\right)_{r=r_0} (r-r_0) + \dots \quad (14)$$

$$\Gamma_0(r) = \Gamma_0(r_0) + \left(\frac{d\Gamma_0}{dr}\right)_{r=r_0} (r-r_0) + \dots \quad (15)$$

Introduction of these expressions into Eq.

(13), followed by integration with the condition that $\bar{v}_1$ and $\bar{v}_2$ are constant, yields

$$\ln [m_1(r)/m_1(r_0)] = -(\omega^2 r_0 / 2RT) \{ [M_1 \bar{v}_1 + \Gamma_0(r_0) M_2 \bar{v}_2] (d\rho_b/dr)_{r=r_0} - M_2 [1 - \bar{v}_2 \rho_b(r_0)] (d\Gamma_0/dr)_{r=r_0} \} (r - r_0)^2 + O[(r - r_0)^3]. \quad (16)$$

Therefore to the approximation that terms higher than $O[(r - r_0)^2]$ are neglected we obtain

$$m_1(r) = m_1(r_0) \exp \left[- \frac{(r - r_0)^2}{2\sigma^2} \right] \quad (17)$$

where σ^2 is given by

$$\sigma^2 = RT / [\omega^2 r_0 \{ [M_1 \bar{v}_1 + \Gamma_0(r_0) M_2 \bar{v}_2] (d\rho_b/dr)_{r=r_0} - M_2 [1 - \bar{v}_2 \rho_b(r_0)] (d\Gamma_0/dr)_{r=r_0} \}] \quad (18)$$

Thus we see that the molality concentration of the macromolecular solute (component 1) distributes in a Gaussian form about the point $r = r_0$ with a standard deviation σ given by Eq. (18).

§ 3. Determination of M_1

Since at $r = r_0$

$$M_1 [1 - \bar{v}_1 \rho_b(r_0)] + \Gamma_0(r_0) M_2 [1 - \bar{v}_2 \rho_b(r_0)] = 0 \quad (19)$$

Eq. (18) may be rewritten

$$\sigma^2 = RT [1 - \bar{v}_2 \rho_b(r_0)] / [M_1 \omega^2 r_0 \{ (\bar{v}_1 - \bar{v}_2) (d\rho_b/dr)_{r=r_0} - M_2 [1 - \bar{v}_2 \rho_b(r_0)]^2 (d\Gamma_0'/dr)_{r=r_0} \}] \quad (20)$$

where Γ_0' stands for $\Gamma_0(M_2/M_1)$. Solution of Eq. (19) for $1/\rho_b(r_0)$ gives

$$1/\rho_b(r_0) = [\bar{v}_1 + \Gamma_0'(r_0) \bar{v}_2] / [1 + \Gamma_0'(r_0)] \quad (21)$$

If there is no thermodynamic interaction between components 1 and 2, $\Gamma_0'(r_0) = 0$ and $(d\Gamma_0'/dr)_{r=r_0} = 0$, so that the expression for σ^2 and $1/\rho_b(r_0)$ reduce to

$$\sigma^2 = RT / [M_1 \omega^2 r_0 \bar{v}_1 (d\rho_b/dr)_{r=r_0}] \quad (22)$$

$$1/\rho_b(r_0) = \bar{v}_1 \quad (23)$$

These equations agree with those derived from the theory of Meselson, Stahl and Vinograd¹⁾ for systems of non-electrolyte components. It is important to note that this agreement is obtained by simply assuming that Γ_0' is zero (at least over short distances about $r = r_0$). In other words, the equations given by Meselson *et al* are applicable provided there is no thermodynamic interaction between the macromolecular solute and the added low-molecular-weight substance, at very low concentrations of the former. Referring to the definition of Γ this condition implies that

$$\lim_{m_1 \rightarrow 0} (\partial \mu_2 / \partial m_1)_{P, m_2} = 0 \quad (24)$$

Since we have the relation

$(\partial \mu_1 / \partial m_2)_{P, m_1} = (\partial \mu_2 / \partial m_1)_{P, m_2}$ (at constant T)
the condition in question may be written

$$\lim_{m_1 \rightarrow 0} (\partial \ln r_1 / \partial m_2)_{P, m_1} = 0 \quad (25)$$

which is less restricted than $r_1 = 1$ as has been assumed in the treatment of Meselson *et al*. Equations (22) and (23) indicate that for a system in which $\Gamma_0' = 0$ both the molecular weight, M_1 , and the partial specific volume, $\bar{v}_1$, of the macromolecular solute can be determined from the measurements of σ and r_0 when the data for $\rho_b(r)$ are obtained from a separate blank experiment. The composition of the third component should be chosen so that a bell-shaped concentration *vs.* distance curve for the macromolecular solute may be observed over some short distance in the central region of the cell. Since M_1 is the quantity to be determined, the concentration of component 1 on the c molality scale may not be known; the quantity measured actually is the concentration on the c scale (grams of solute per ml. of solution) as a function of r . However it can be shown that for solutions sufficiently dilute in component 1 (though not necessarily dilute in component 2) the quantity dm_1/dr will ap-

proach zero as dc_1/dr approaches zero, where c_1 is the concentration of component 1 on the scale. Thus for solutions with which we are concerned in the present paper the maximum will occur at the same point in the cell for both the c_1 vs. r and the m_1 vs. r curves. To the same approximation the value of σ may be determined from the actually measured c_1 vs. r curve. The use of the above method is possible only when the concentration distribution of the macromolecular solute can be measured independently. However, this is not often the case.

In cases when Γ_0' is not zero this type of experiment generally does not allow to determine M_1 and $\bar{v}_1$, because Γ_0' cannot be measured. However, if Γ_0' is constant at least over a short interval about $r=r_0$, and if $\bar{v}_1$ and $\bar{v}_2$ can be determined separately, the values of M_1 and $\Gamma_0'(r_0)$ may be calculated from measurements of σ , r_0 , $\rho_b(r_0)$, and $(d\rho_b/dr)_{r=r_0}$. First, substitution of the values of $\rho_b(r_0)$, $\bar{v}_1$, and $\bar{v}_2$ into Eq. (21) yields the desired value of $\Gamma_0'(r_0)$. Next, since

$$(d\Gamma_0'/dr)_{r=r_0}=0$$

under the condition mentioned above, Eq. (20) may be solved for M_1 to give

$$M_1 = \frac{RT[1 - \bar{v}_2 \rho_b(r_0)]}{\sigma^2 \omega^2 r_0 (\bar{v}_1 - \bar{v}_2) (d\rho_b/dr)_{r=r_0}} \quad (26)$$

Hence M_1 can be determined if the above-mentioned experimental data are available.

Thus we see that there is the possibility that we can evaluate the molecular weight of a macromolecule from sedimentation equilibrium experiments with a mixed solvent, in the case when we have reason to believe that Γ_0' varies slowly with r . According to the usual type of sedimentation equilibrium experiment, the molecular weight of a solute dissolved in a mixed solvent can be determined unambiguously only when Γ_0' is zero throughout the cell.²⁾ The condition $d\Gamma_0'/dr=0$ (for all r)* is apparently less restricted than the condition $\Gamma_0'=0$ (for all r).

References

- 1) M. Meselson, F. W. Stahl and J. R. Vinograd: Proc. Nat. Acad. Sci. U. S. **43** (1957) 581.
- 2) J. W. Williams, K. E. Van Holde, R. L. Baldwin and H. Fujita: Chem. Rev. **58** (1958) 715.

* For Eq. (26) to be valid the condition

$$(d\Gamma_0'/dr)_{r=r_0}=0$$

is sufficient, but since r_0 is unknown in advance, it is safe to impose a more restricted condition $d\Gamma_0'/dr=0$ for all r .

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 2, FEBRUARY, 1960

Maxwell's Formula for Three-Dimensional and Large Deformation

By Wataru SEGAWA

College of Humanities and Sciences, Nihon University, Tokyo

(Received November 12, 1959)

Classical Maxwell's formula in the case of a single relaxation time is extended so as to be applicable to three-dimensional and large deformation. It is also shown that for small deformations the derived formula is reduced to Alfrey's formula which is valid for three-dimensional and small deformation.

Application to simple elongation is shown to be satisfactory.

§ 1. Introduction

As is well-known, classical Maxwell's formula having a single relaxation time can be derived from a mechanical model, series

combination of a Hookian spring and a Newtonian dashpot, and is not valid for three-dimensional and large deformation.

It seems that so far main efforts to improve

Maxwell's formula have been directed to the problem of, for example, combined models, relaxation spectra etc. and not how to make Maxwell's formula applicable to general deformation, even though Alfrey¹⁾ derived general formula for three-dimensional and small deformation and some authors²⁾³⁾⁴⁾ concerned with large elastico-viscous deformation.

In this article, we will derive Maxwell's formula for three-dimensional and large deformation of initially isotropic material, in a different way from the above articles, and an application of the derived formula to simple elongation will be done. It will be also shown that Alfrey's formula can be derived from our formula, using the assumption that the deformation is small.

§ 2. Strain and Strain Rate

Let the position of a material particle of a system of particles be x^i for undeformed state ($t=0$) and x^{*i} for deformed state ($t=t$), on a rectangular coordinate system $X^i (i=1, 2, 3)$ fixed in space. Then, we can define two measures of finite strain, for latter use, as follows:

$$e_{\lambda\mu}^G = \frac{1}{2}(g'^{\lambda\mu} - \delta_{\lambda\mu}) \quad g'^{\lambda\mu} = x_{,i}^{*\lambda} x_{,i}^{*\mu} \quad (2.1)$$

$$e_{ij} = \frac{1}{2}(\delta_{ij} - g^{ij}) \quad g^{ij} = x_{,\lambda}^i x_{,\lambda}^j \quad (2.2)$$

where $x_{,i}^{*\lambda} = \partial x^{*\lambda} / \partial x^i$, $x_{,\lambda}^i = \partial x^i / \partial x^{*\lambda}$ etc.

Using the above definitions, we can easily prove that

$$e_{ij} = x_{,\lambda}^i x_{,\mu}^j e_{\lambda\mu}^G \quad (2.3)$$

$$e_{\lambda\mu}^G = x_{,i}^{*\lambda} x_{,j}^{*\mu} e_{ij} \quad (2.4)$$

Strain rate tensor $f_{\lambda\mu}$ can be defined as follows:

$$f_{\lambda\mu} = x_{,i}^{*\lambda} x_{,j}^{*\mu} \dot{e}_{ij} \quad (2.5)$$

$$\dot{e}_{ij} = x_{,\lambda}^i x_{,\mu}^j f_{\lambda\mu} \quad (2.6)$$

Let the X^λ -component of the velocity v of a material particle in time t be v^λ , then $f_{\lambda\mu}$ is also defined by, as ordinarily done,

$$f_{\lambda\mu} = \frac{1}{2}(v_{,\mu}^\lambda + v_{,\lambda}^\mu) \quad (2.7)$$

where

$$v_{,\mu}^\lambda = \partial v^\lambda / \partial x^{*\mu} \text{ etc. and } v_{,\lambda}^\lambda = dx^{*\lambda} / dt \text{ etc.} \quad (2.8)$$

We can easily prove that the right-hand side of Eq (2.5) is equivalent to that of Eq. (2.7), using Eq. (2.8).

From Eq. (2.3) and (2.5), we have

$$f_{\lambda\mu} = x_{,i}^{*\lambda} x_{,j}^{*\mu} \frac{d}{dt} \left(x_{,\alpha}^i x_{,\beta}^j e_{\alpha\beta}^G \right) \quad (2.9)$$

We will use this equation to represent elastic strain rate-elastic stress relation.

§ 3. Strain Rate-Stress Relation

i) Viscous liquid

Reiner⁵⁾ derived strain rate-stress relation of a viscous liquid which is isotropic in its rest state. This relation can be written as follows using the notations of this article:

$$f_{\lambda\mu} = G_0 \delta_{\lambda\mu} + G_1 T^{\lambda\mu} + G_2 T^{\lambda\gamma} T^{\gamma\mu} \quad (3.1)$$

where G_0, G_1 and G_2 are functions of stress invariants defined by

$$T_1 = T^{\lambda\lambda}, \quad T_2 = \frac{1}{2} T^{\lambda\mu} T^{\lambda\mu}, \quad T_3 = \frac{1}{6} T^{\lambda\gamma} T^{\gamma\mu} T^{\mu\lambda} \quad (3.2)$$

ii) Elastic solid

Reiner⁶⁾ derived stress-strain relation of an elastic solid which is isotropic in its initial state, as follows:

$$T^{\lambda\mu} = H_0 \delta_{\lambda\mu} + H_1 e_{\lambda\mu} + H_2 e_{\lambda\gamma} e_{\gamma\mu} \quad (3.3)$$

where H_0, H_1 and H_2 are functions of strain invariants.

Analogously, using the principle of generalized dimensions, we can derive strain-stress relation of an isotropic body, which, using $e_{\lambda\mu}^G$ as measure of strain, will be expressed as follows:

$$e_{\lambda\mu}^G = F_0 \delta_{\lambda\mu} + F_1 T^{\lambda\mu} + F_2 T^{\lambda\gamma} T^{\gamma\mu} \quad (3.4)$$

where F_0, F_1 and F_2 are functions of stress invariants.

Substituting Eq. (3.4) into Eq. (2.9), we have

$$f_{\lambda\mu} = x_{,i}^{*\lambda} x_{,j}^{*\mu} \frac{d}{dt} \left\{ x_{,\alpha}^i x_{,\beta}^j (F_0 \delta_{\alpha\beta} + F_1 T^{\alpha\beta} + F_2 T^{\alpha\gamma} T^{\gamma\beta}) \right\} \quad (3.5)$$

This equation expresses strain rate-stress relation of an elastic solid which is initially isotropic.

§ 4. Maxwell's Formula

Let us regard a Maxwellian material as a system of particles, then the displacement of a material particle from x^i (initial position) to x^{*i} (final position) will be done by both elastic and viscous process.

In analogy with classical model, we assume that

i) actual strain rate is a sum of elastic strain rate and viscous strain rate,

ii) elastic stress is equivalent to viscous

stress and also to actual stress.

Then, from Eq. (3.1) and (3.5), we have

$$f_{\lambda\mu} = \frac{\partial y^{*\lambda}}{\partial x^i} \frac{\partial y^{*\mu}}{\partial x^j} \frac{d}{dt} \left\{ \frac{\partial x^i}{\partial y^{*\alpha}} \frac{\partial x^j}{\partial y^{*\beta}} \times \right. \\ \left. (F_0 \delta_{\alpha\beta} + F_1 T^{\alpha\beta} + F_2 T^{\alpha\gamma} T^{\gamma\beta}) \right\} \\ + G_0 \delta_{\lambda\mu} + G_1 T^{\lambda\mu} + G_2 T^{\lambda\gamma} T^{\gamma\mu} \quad (4.1)$$

which is Maxwell's formula for three-dimensional and large deformation of an initially isotropic body. If the material is incompressible, additional condition

$$\operatorname{div} \mathbf{v} = f_{\lambda\lambda} = 0 \quad (4.2)$$

must hold. We must notice that this equations artificial coordinates $y^{*\lambda}$ which express the final position when only elastic process took place. So, it is necessary for us to decide, beforehand, $\partial y^{*\lambda}/\partial x^i \cdot \partial y^{*\mu}/\partial x^j$ and $\partial x^i/\partial y^{*\alpha} \cdot \partial x^j/\partial y^{*\beta}$ as function of stress. Eq. (3.4) and (2.1) will work for this decision, together with other conditions. An example of calculation will be shown in § 5.

Let the x^λ (or x^i) component of an elastic displacement be u^λ (or u^i), then we have

$$\frac{\partial y^{*\lambda}}{\partial x^i} \frac{\partial y^{*\mu}}{\partial x^j} = \frac{\partial}{\partial x^i} (x^\lambda + u^\lambda) \frac{\partial}{\partial x^j} (x^\mu + u^\mu) \\ = (\delta_{\lambda i} + u_{,i}^\lambda) (\delta_{\mu j} + u_{,j}^\mu), \quad (4.3)$$

$$\frac{\partial x^i}{\partial y^{*\alpha}} \frac{\partial x^j}{\partial y^{*\beta}} = \frac{\partial}{\partial y^{*\alpha}} (y^{*i} - u^i) \frac{\partial}{\partial y^{*\beta}} (y^{*j} - u^j) \\ = (\delta_{i\alpha} - u_{,\alpha}^i) (\delta_{j\beta} - u_{,\beta}^j). \quad (4.4)$$

When elastic deformation is sufficiently small, we can neglect the higher order terms of displacement gradients compared to the lower order terms of those, and strain-stress relation will become linear. Then, Eq. (4.3) and Eq. (4.4) will become

$$\frac{\partial y^{*\lambda}}{\partial x^i} \frac{\partial y^{*\mu}}{\partial x^j} = \delta_{\lambda i} \delta_{\mu j}, \quad (4.5)$$

$$\frac{\partial x^i}{\partial y^{*\alpha}} \frac{\partial x^j}{\partial y^{*\beta}} = \delta_{i\alpha} \delta_{j\beta}. \quad (4.6)$$

Substituting Eq. (4.5) Eq. (4.6) into Eq. (4.1) and using linear strain-stress relation we have

$$\left. \begin{aligned} \frac{\dot{\alpha}}{\alpha} &= \left(\frac{\partial y^{*1}}{\partial x^1} \right)^2 \frac{d}{dt} \left\{ \left(\frac{\partial x^1}{\partial y^{*1}} \right)^2 (F_0 + F_1 T^{11} + F_2 T^{112}) \right\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ &- \frac{1}{2} \frac{\dot{\alpha}}{\alpha} = \left(\frac{\partial y^{*2}}{\partial x^2} \right)^2 \frac{d}{dt} \left\{ \left(\frac{\partial x^2}{\partial y^{*2}} \right)^2 F_0 \right\} + G_0 \end{aligned} \right\} \quad (5.3)$$

$$f_{\lambda\mu} = \frac{d}{dt} (F_0 \delta_{\lambda\mu} + F_1 T^{\lambda\mu}) \\ + G_0 \delta_{\lambda\mu} + G_1 T^{\lambda\mu} + G_2 T^{\lambda\gamma} T^{\gamma\mu}, \quad (4.7)$$

where, denoting shear modulus as μ ,

$$F_0 = -\frac{1}{6\mu} T_1, \quad F_1 = \frac{1}{2\mu}. \quad (4.8)$$

This is Maxwell's formula for small elastic and large viscous deformation of an initially isotropic material.

If viscous strain rate is also sufficiently small, viscous deformation for definite time interval will also become small, and strain rate-stress relation will become linear. Then, Eq. (4.7) will be reduced to

$$f_{\lambda\mu} = \frac{d}{dt} (F_0 \delta_{\lambda\mu} + F_1 T^{\lambda\mu}) + G_0 \delta_{\lambda\mu} + G_1 T^{\lambda\mu} \quad (4.9)$$

where, denoting shear modulus by μ and coefficient of viscosity by η ,

$$\left. \begin{aligned} F_0 &= -\frac{1}{6\mu} T_1, & F_1 &= \frac{1}{2\mu}, \\ G_0 &= -\frac{1}{6\eta} T_1, & G_1 &= \frac{1}{2\eta}. \end{aligned} \right\} \quad (4.10)$$

Eq. (4.9), together with Eq. (4.10), is equivalent to Alfrey's formula.¹⁾

In the next paragraph, application of Eq. (4.1) to the well-known problems of a simple elongation will be done. Their results under the assumption that deformation is small could be derived also from Eq. (4.9) directly.

§ 5. Simple Elongation

Let us consider incompressible uniform elongation in the direction of X^1 -axis. Denoting the extension ratio by α , this deformation is specified by

$$x^{*1} = \alpha x^1, \quad x^{*2} = \frac{1}{\sqrt{\alpha}} x^2, \quad x^{*3} = \frac{1}{\sqrt{\alpha}} x^3. \quad (5.1)$$

Then, from Eq. (2.7) and Eq. (2.8), we have⁷⁾

$$f_{11} = \frac{\dot{\alpha}}{\alpha}, \quad f_{22} = f_{33} = -\frac{1}{2} \frac{\dot{\alpha}}{\alpha}, \\ \text{all others} = 0. \quad (5.2)$$

We assume that stress components vanish except T^{11} , as ordinarily done in simple elongation. Then, Eq. (4.1) results in

and from Eq. (3.2) we have

$$T_1 = T^{11}, \quad T_2 = \frac{1}{2}(T^{11})^2, \quad T_3 = \frac{1}{3}(T^{11})^3, \quad (5.4)$$

from which we can see that F_0, F_1, F_2 are functions of T^{11} alone.

From Eq. (3.4), we have

$$\left. \begin{aligned} \frac{1}{2} \left\{ \left(\frac{\partial y^{*1}}{\partial x^1} \right)^2 - 1 \right\} &= F_0 + F_1 T^{11} + F_2 T^{112} \\ \frac{1}{2} \left\{ \left(\frac{\partial y^{*2}}{\partial x^2} \right)^2 - 1 \right\} &= F_0 \end{aligned} \right\} \quad (5.5)$$

Eq. (5.1) shows that $x^{*\lambda}$ is a function of x^λ alone, so we can assume that $y^{*\lambda}$ is a function of x^λ alone. Then, substituting Eq. (5.5) into Eq. (5.3), we have

$$\left. \begin{aligned} \frac{\dot{\alpha}}{\alpha} &= \{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1\} \frac{d}{dt} \left\{ \frac{F_0 + F_1 T^{11} + F_2 T^{112}}{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1} \right\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} &= (2F_0 + 1) \frac{d}{dt} \left\{ \frac{F_0}{2F_0 + 1} \right\} + G_0 \end{aligned} \right\} \quad (5.6)$$

$$\therefore \left. \begin{aligned} \frac{\dot{\alpha}}{\alpha} &= \frac{1}{2} \frac{d}{dt} \ln \{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} &= \frac{1}{2} \frac{d}{dt} \ln (2F_0 + 1) + G_0 \end{aligned} \right\} \quad (5.7)$$

i) When $T^{11} = \text{const.}$

From Eq. (5.7), we have

$$\frac{\dot{\alpha}}{\alpha} = G_0 + G_1 T^{11} + G_2 T^{112}, \quad -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} = G_0. \quad (5.8)$$

Then, we obtain

$$\alpha = \alpha_0 \exp \frac{2}{3}(G_1 T^{11} + G_2 T^{112})t \quad (5.9)$$

$$\text{or } \ln \alpha = \ln \alpha_0 + \frac{2}{3}(G_1 T^{11} + G_2 T^{112})t \quad (5.9')$$

Eq. (5.9') tells us that the logarithm of extension ratio is proportional to time t but the time derivative of $\ln \alpha$ is not proportional to T^{11} or α_0 . This facts agree well with experimental results⁸⁾ for some substances.

When deformation is small, that is,

$$\ln \alpha = \ln(1 + \varepsilon) \doteq \varepsilon, \quad G_2 = 0, \quad G_1 = \text{const} = 1/2\eta$$

Eq. (5.9') is reduced to

$$\varepsilon = \varepsilon_0 + \frac{T^{11}}{3\eta}t \quad (5.10)$$

which is equivalent to the results derived from classical Maxwell's formula.

ii) When $\alpha = \text{const}$

From Eq. (5.7), we have

$$\left. \begin{aligned} \frac{1}{2} \frac{d}{dt} \ln \{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1\} \\ + G_0 + G_1 T^{11} + G_2 T^{112} &= 0 \\ \frac{1}{2} \frac{d}{dt} \ln (2F_0 + 1) + G_0 &= 0 \end{aligned} \right\} \quad (5.11)$$

We cannot solve this equation analytically without introducing any assumption.

If deformation is small, we have

$$\left. \begin{aligned} \frac{1}{2} \frac{d}{dt} \{2(F_0 + F_1 T^{11})\} + G_0 + G_1 T^{11} &= 0 \\ \frac{1}{2} \frac{d}{dt} \{2F_0\} + G_0 &= 0 \end{aligned} \right\} \quad (5.12)$$

$$\therefore \frac{d}{dt}(F_1 T^{11}) + G_1 T^{11} = 0 \quad (5.13)$$

where $F_1 = \text{const} = 1/2\mu$, $G_1 = \text{const} = 1/2\eta$

Then, we have

$$T^{11} = T_0^{11} e^{-(\mu/\eta)t} \quad (5.14)$$

which is equivalent to classical results.

iii) When $\dot{\alpha} = \infty$

From Eq. (5.7), we have

$$\left. \begin{aligned} \frac{1}{\alpha} &= \frac{1}{2} \frac{d}{d\alpha} \ln \{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1\} \\ -\frac{1}{2} \frac{1}{\alpha} &= \frac{d}{d\alpha} \ln (2F_0 + 1) \\ \therefore 2 \ln \alpha &= \ln \{2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1\} \\ -\ln \alpha &= \ln (2F_0 + 1) \end{aligned} \right\}$$

where we have assumed that $\alpha = 1$ when $T^{11} = 0$.

$$\therefore \alpha^2 = 2(F_0 + F_1 T^{11} + F_2 T^{112}) + 1 \quad \left. \begin{aligned} \frac{1}{\alpha} &= 2F_0 + 1 \end{aligned} \right\} \quad (5.15)$$

$$\therefore \alpha^2 - \frac{1}{\alpha} = 2(F_1 T^{11} + F_2 T^{112}) \quad (5.16)$$

$$\text{or } T^{11} = f\left(\alpha^2 - \frac{1}{\alpha}\right) \quad (5.16')$$

If $F_2 = 0$, $F_1 = 1/2\mu$, we have

$$T^{11} = \mu\left(\alpha^2 - \frac{1}{\alpha}\right)$$

Actual stress is related to conventional stress p^{11} by $T^{11} = \alpha p^{11}$. Then

$$p^{11} = \mu\left(\alpha - \frac{1}{\alpha^2}\right) \quad (5.17)$$

which is equivalent to the well-known stress-strain relation of rubber-like substances.

Moreover, if $\alpha - 1 = \varepsilon \ll 1$, we have

$$T^{11} = \mu\{(1 + \varepsilon)^2 - (1 + \varepsilon)^{-1}\} = 3\mu\varepsilon \quad (5.18)$$

which represents Hooke's law.

§ 6. Another Expression of Maxwell's Formula

In the preceding treatment, we have used $e_{\lambda\mu}^A$ and e_{ij} defined by Eq. (2.1) and Eq. (2.2) respectively. Let us show that, instead of them, we can use $e_{\lambda\mu}^A$ and e_{ij}^L defined

$$e_{\lambda\mu}^A = \frac{1}{2}(\delta_{\lambda\mu} - g_{\lambda\mu}) \quad g_{\lambda\mu} = x_{,\lambda}^k x_{,\mu}^k \quad (6.1)$$

$$e_{ij}^L = \frac{1}{2}(g_{ij} - \delta_{ij}) \quad g_{ij} = x_{,i}^{*\nu} x_{,j}^{*\nu} \quad (6.2)$$

From the above definitions, we can easily prove that

$$e_{ij}^L = x_{,i}^{*\lambda} x_{,j}^{*\mu} e_{\lambda\mu}^A \quad (6.3) \quad e_{\lambda\mu}^A = x_{,\lambda}^i x_{,\mu}^j e_{ij}^L \quad (6.4)$$

and

$$f_{\lambda\mu} = x_{,\lambda}^i x_{,\mu}^j \dot{e}_{ij}^L \quad (6.5) \quad \dot{e}_{ij}^L = x_{,i}^{*\lambda} x_{,j}^{*\mu} f_{\lambda\mu} \quad (6.6)$$

From Eq. (6.3) and Eq. (6.5), we have

$$f_{\lambda\mu} = x_{,\lambda}^i x_{,\mu}^j \frac{d}{dt} (x_{,i}^{*\alpha} x_{,j}^{*\beta} e_{\alpha\beta}^A) \quad (6.7)$$

Strain-stress relation is written as

$$e_{\lambda\mu}^A = F_0' \delta_{\lambda\mu} + F_1' T^{\lambda\mu} + F_2' T^{\lambda\nu} T^{\nu\mu} \quad (6.8)$$

Substituting Eq. (6.8) into Eq. (6.7), we have

$$f_{\lambda\mu} = x_{,\lambda}^i x_{,\mu}^j \frac{d}{dt} \{x_{,i}^{*\alpha} x_{,j}^{*\beta} (F_0' \delta_{\alpha\beta} + F_1' T^{\alpha\beta} + F_2' T^{\alpha\gamma} T^{\gamma\beta})\} \quad (6.9)$$

which expresses strain rate-stress relation of an elastic solid.

Then, Maxwell's formula will be

$$f_{\lambda\mu} = \frac{\partial x^i}{\partial y^{*\lambda}} \frac{\partial x^j}{\partial y^{*\mu}} \frac{d}{dt} \times \left\{ \frac{\partial v^{*\alpha}}{\partial x^i} \frac{\partial y^{*\beta}}{\partial x^j} (F_0' \delta_{\alpha\beta} + F_1' T^{\alpha\beta} + F_2' T^{\alpha\gamma} T^{\gamma\beta}) \right\} + G_0 \delta_{\lambda\mu} + G_1 T^{\lambda\mu} + G_2 T^{\lambda\nu} T^{\nu\mu} \quad (6.10)$$

Let us apply Eq. (6.10) to the case of a simple elongation. Analogously with § 5, we have, from Eq. (6.10),

$$\left. \begin{aligned} \frac{\dot{\alpha}}{\alpha} &= \left(\frac{\partial x^1}{\partial y^{*1}} \right)^2 \frac{d}{dt} \left\{ \left(\frac{\partial y^{*1}}{\partial x^1} \right)^2 (F_0' + F_1' T^{11} + F_2' T^{112}) \right\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} &= \left(\frac{\partial x^2}{\partial y^{*2}} \right)^2 \frac{d}{dt} \left\{ \left(\frac{\partial y^{*2}}{\partial x^2} \right)^2 F_0' \right\} + G_0 \end{aligned} \right\} \quad (6.11)$$

and from Eq. (6.8)

$$\left. \begin{aligned} \frac{1}{2} \left\{ 1 - \left(\frac{\partial x^1}{\partial y^{*1}} \right)^2 \right\} &= F_0' + F_1' T^{11} + F_2' T^{112} \\ \frac{1}{2} \left\{ 1 - \left(\frac{\partial x^2}{\partial y^{*2}} \right)^2 \right\} &= F_0' \end{aligned} \right\} \quad (6.12)$$

Substituting Eq. (6.12) into Eq. (6.11), we have

$$\left. \begin{aligned} \frac{\dot{\alpha}}{\alpha} &= \{1 - 2(F_0' + F_1' T^{11} + F_2' T^{112})\} \frac{d}{dt} \left\{ \frac{F_0' + F_1' T^{11} + F_2' T^{112}}{1 - 2(F_0' + F_1' T^{11} + F_2' T^{112})} \right\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} &= (1 - 2F_0') \frac{d}{dt} \left\{ \frac{F_0'}{1 - 2F_0'} \right\} + G_0 \end{aligned} \right\} \quad (6.13)$$

$$\left. \begin{aligned} \therefore \frac{\dot{\alpha}}{\alpha} &= -\frac{1}{2} \frac{d}{dt} \ln \{1 - 2(F_0' + F_1' T^{11} + F_2' T^{112})\} + G_0 + G_1 T^{11} + G_2 T^{112} \\ -\frac{1}{2} \frac{\dot{\alpha}}{\alpha} &= -\frac{1}{2} \frac{d}{dt} \ln \{1 - 2F_0'\} + G_0 \end{aligned} \right\} \quad (6.14)$$

which corresponds to Eq. (5.7).

We can easily show that using Eq. (6.14) we can derive the similar results as i), ii), iii) in §5, and we can see that Eq. (6.10) can play the role of Eq. (4.1). Moreover, we could derive any other expression of Maxwell's formula, if there exists any measure of finite strain from which we constitute elastic strain rate-elastic stress relation, or more generally, only if we could have any elastic strain rate-elastic stress relation.

§7. Conclusions and Discussions

In the precedings, generalized Maxwell's formula have been derived, which is valid for three-dimensional and large deformation of an initially isotropic material. This formula will be reduced to general strain-stress relation of isotropic elastic solid when the terms relating to viscosity are absent and to general strain rate-stress relation of an isotropic viscous liquid when the terms relating to elasticity are neglected. We could say that our Maxwell model is a series combination of a generalized spring (non-Hookian spring) and a generalized dashpot (non-Newtonian dashpot).

Our formula contains artificial coordinates (elastic coordinates) and their gradients which, in general, cannot be observed directly. As in Maxwell model elastic stress is equivalent to actual (observable) stress, we can decide elastic coordinate or their gradients as functions of actual stress, by virtue of strain-stress relation of an elastic solid. But, this decision is not always easy, without any other conditions which simplify the calculations.

We could have other expression of generalized Maxwell's formula, only if we had any other strain rate-stress relation of an elastic solid which is valid for large deformation.

References

- 1) For example, T. Alfrey: *Mechanical Behaviors of High Polymer* (Interscience Publ, New York, 1948) 208.
- 2) W. Segawa: J. Phys. Soc. Japan **12** (1957) 996.
- 3) Yoh-Han Pao: J. Appl. Phys. **28** (1957) 591.
- 4) M. Yamamoto: J. Phys. Soc. Japan **14** (1959) 313.
- 5) M. Reiner: Amer. J. Math. **67** (1945) 350.
- 6) M. Reiner: Amer. J. Math. **70** (1948) 43.
- 7) W. Segawa: J. Phys. Soc. Japan **14** (1959) 1102.
- 8) M. D. Stern and A. V. Tobolsky: J. Chem. Phys. **14** (1946) 93.

Ultrasonic Propagation through Aqueous Solutions of Acetates

By M. KRISHNAMURTHI* and M. SURYANARAYANA

Physical Laboratories, Osmania University, Hyderabad-7, India

(Received October 1, 1959)

Using the pulse method in the range of 2 to 26 Mc/s the ultrasonic absorption, velocity and the adiabatic compressibility have been studied in eleven aqueous acetate solutions up to a concentration of 1 mole/litre. The substances studied are the acetates of lithium, sodium, potassium, ammonium, magnesium, calcium, strontium, barium, zinc, cadmium and lead. Absorption in mercuric acetate has been studied only at 2 and 6 Mc/s. Two regions of relaxation are noticed, one below 10 Mc/s and the other between 10 and 26 Mc/s. The first relaxation is ascribed to the dissociation reaction of the salt and the second one to the monomer-dimer reaction of the acetic acid formed by the hydrolysis of the salt in water.

§ Introduction

Ultrasonic relaxation phenomena have been observed by the authors in aqueous solutions of some gases and salts and are reported in earlier papers^{1,2}. These include solutions of gases like sulphur dioxide and nitrogen tetroxide and also of sulphites, bi-sulphites and nitrites in water. As a continuation of the same work the ultrasonic propagation in a number of aqueous acetate solutions have been studied and the results are reported in this paper. A preliminary report of this work by the authors³ has been published earlier.

Some of the acetate solutions were studied by earlier workers. Thus Bazulin⁴ working in the frequency range of 7 to 30 Mc/s found that $\alpha\lambda$, the excess absorption per wavelength, in aqueous zinc acetate solutions passes through a maximum near 8 Mc/s for concentrations of the order of 0.1 mole/litre. Berrett, Beyer and McNamara⁵ have studied the aqueous solutions of sodium, potassium and copper acetates. In the case of copper acetate solutions they found the relaxation peaks of absorption near 18 Mc/s for concentrations between 0.1 and 0.3 moles/litre. They infer from their work that in the case of sodium and potassium acetate solutions the peaks of excess absorption per wavelength will occur below 10 Mc/s.

§ 2. Experimental Method

The experimental procedure adopted is the

* Now at the Indian Institute of Science, Bangalore, India.

pulse method as reported in the earlier papers and covers a range of 2 to 26 Mc/s. The measurements are confined to the Fresnel region of the ultrasonic beam in the medium. The error in the measurement of absorption is estimated to be better than ± 5 per cent at the lower frequencies and ± 3 per cent at the higher frequencies.

The ultrasonic velocity is measured at 6.36 Mc/s with the help of the movable time mark of a DuMont oscilloscope 256 F by registering the two positions of the received pulse as the receiver is moved accurately through a known distance. The velocity is measured to an accuracy of ± 1 meter/sec. The densities of the solutions are determined in the laboratory and the adiabatic compressibility is calculated from a knowledge of the ultrasonic velocity and the density of the solution.

Aqueous solutions of lithium, sodium, potassium, ammonium, magnesium, calcium, strontium, barium, zinc, cadmium and lead acetates have been studied upto a concentration of 1 mole/litre at seven different frequencies, namely, 2.12, 5.02, 6.36, 10.61, 15.49, 19.82 and 25.81 Mc/s. The salts used are analytical reagents of guaranteed purity. All the results refer to the room temperature of $28^\circ \pm 1^\circ \text{C}$. The alignment of the crystals is tested by verifying with distilled water the values of absorption and velocity. This check is made everytime when measurements are taken at a given frequency on a given substance.

Table I. Ultrasonic velocity (meters/sec)
Temperature: 29°C

Conc. Moles/litre	Lithium Acetate	Sodium Acetate	Potassium Acetate	Ammonium Acetate	Magnesium Acetate	Calcium Acetate	Strontium Acetate	Barium Acetate	Zinc Acetate	Cadmium Acetate	Lead Acetate	Mercuric Acetate
1.0	1575	1577	1584	1570	1643	1596	1603	1588	1532	—	1451	—
0.8	1550	1570	1556	1557	1613	1579	1595	1578	1529	1558	1456	1488
0.6	1540	1555	1542	1546	1589	1561	1575	1566	1525	1560	1465	1466
0.4	1527	1532	1524	1537	1562	1544	1556	1556	1524	1558	1485	1478
0.2	1520	1519	1518	1525	1540	1527	1542	1542	1524	1554	1498	1489
0	1510	1510	1510	1510	1510	1510	1510	1510	1510	1510	1510	1510

Table II. Adiabatic compressibility (in 10^{-12} cm²/dyne)
Temperature: 29°C

Conc. Moles/litre	Lithium Acetate	Sodium Acetate	Potassium Acetate	Ammonium Acetate	Magnesium Acetate	Calcium Acetate	Strontium Acetate	Barium Acetate	Zinc Acetate	Cadmium Acetate	Lead Acetate	Mercuric Acetate
1.0	39.25	38.81	38.14	40.05	34.67	36.42	34.44	33.94	38.42	—	38.83	—
0.8	40.74	39.68	40.17	40.86	36.32	37.77	35.85	35.37	39.32	37.03	39.96	38.82
0.6	41.56	40.76	41.41	41.60	38.04	39.22	37.45	36.87	40.31	37.92	41.18	41.35
0.4	42.43	42.07	42.38	42.42	40.04	40.70	39.37	38.84	41.29	38.98	41.83	42.27
0.2	43.08	43.24	43.10	43.20	41.87	42.34	41.42	41.06	42.27	40.18	42.89	43.27
0	43.66	43.66	43.66	43.66	43.66	43.66	43.66	43.66	43.66	43.66	43.66	43.66

§ 3. Results

The ultrasonic velocities determined for these solutions are recorded in Table I. The adiabatic compressibilities, calculated from these velocities and the corresponding densities, are shown in Table II.

The excess absorption, over and above that due to viscosity and thermal conduction, is calculated for each solution at every concentration from the experimentally determined values of α/f^2 . The coefficients of viscosity of the solutions required in this connection are taken from the International Critical Tables vol. V, 1929. The absorption in zinc and cadmium acetate solutions is so large that the viscosity contribution to absorption is neglected in these two cases. The contribution of thermal conductivity of the solutions to the classical absorption is neglected as it is usually a small fraction of the viscosity contribution. The excess absorption per wavelength ($\alpha\lambda$) calculated from these results are shown graphically (figures 1 and 2) in some cases and in the Tables III and IV

for some others.

§ 4. Discussion of the Results

(a) *Velocity and compressibility*: With the exception of the heavy metal acetates, namely, lead and mercuric acetate solutions, the ultrasonic velocity in all the other ten acetate solutions is found to increase with increase of concentration. The decrease of velocity with increase of concentration for lead acetate solutions is in conformity with the earlier observation on the same by Balachandran⁹. The ultrasonic velocity in zinc acetate solution, even at a concentration of 1 mole/litre, is not much different from that of water. Besides, the variation of velocity with concentration is not significant beyond 0.2 moles/litre. This observation holds also for cadmium acetate solutions. This is interesting in view of the extremely large ultrasonic absorption observed in these solutions. As for the remaining acetate solutions it is seen that, for any given concentration, the univalent acetates generally show lesser velocity than

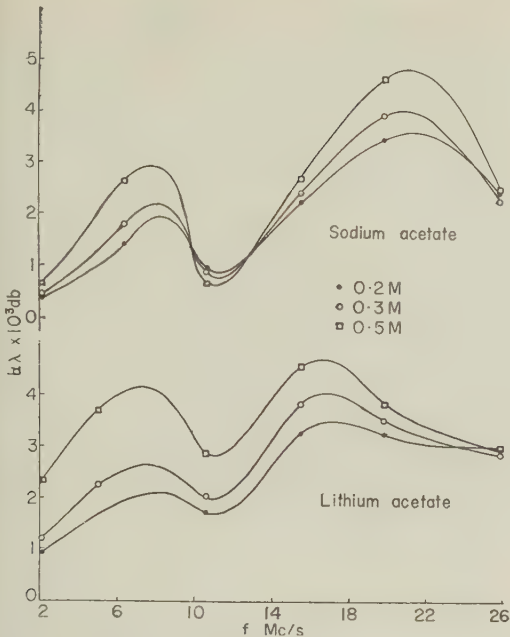


Fig. 1. Dependence of $\alpha\lambda$, the ultrasonic absorption per wavelength, on the frequency in aqueous solutions of sodium and lithium acetates at concentrations of 0.2; 0.3 and 0.5 moles per litre.

Table III. Ultrasonic absorption per wavelength in units of 10^{-3} db

Substance	Conc. moles/litre	Frequency in Mc/s						
		2.12	5.02	6.36	10.61	15.49	19.82	25.81
Potassium Acetate	0.8	0.56	1.59	1.73	1.18	4.94	4.81	3.20
	0.5	0.34	0.87	1.03	1.24	4.22	3.58	2.89
	0.3	0.29	0.72	0.91	1.27	3.62	3.10	2.90
	0.2	0.29	0.61	0.90	1.29	3.16	3.06	2.92
Ammonium Acetate	0.8	1.07	1.93	3.25	2.43	4.13	3.97	4.49
	0.5	0.57	1.15	1.85	1.96	3.21	3.36	3.37
	0.3	0.41	0.85	1.27	1.66	2.84	3.21	2.39
	0.2	0.34	0.77	1.08	1.47	2.56	3.05	2.03
Magnesium Acetate	0.8	1.41	5.71	9.28	4.89	7.30	9.50	6.75
	0.5	0.82	2.98	4.89	2.47	5.69	6.42	4.51
	0.3	0.55	1.80	2.65	1.66	4.70	4.36	4.04
	0.2	0.46	1.33	1.77	1.50	4.09	3.59	3.85
Barium Acetate	0.8	39.8	16.6	15.1	10.2	23.4	29.1	22.3
	0.5	21.5	8.0	7.1	3.7	15.5	14.3	9.3
	0.3	12.1	5.6	3.7	2.3	10.1	8.1	6.1
	0.2	7.5	4.1	3.2	2.1	7.8	6.3	5.4

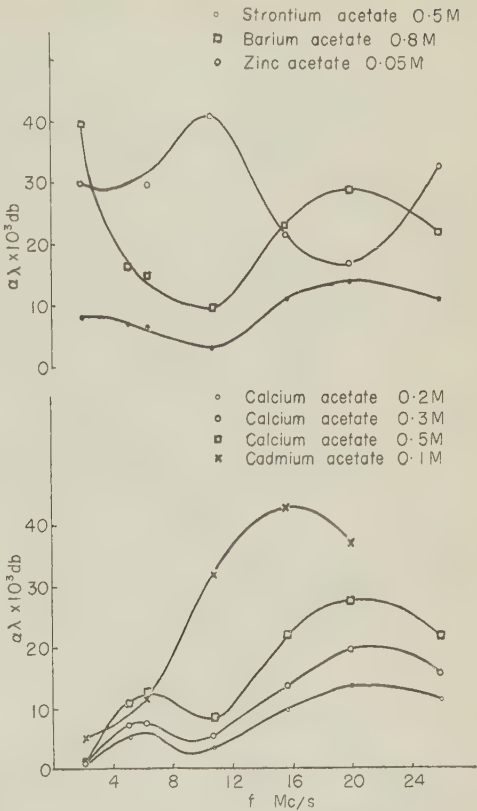


Fig. 2. Dependence of $\alpha\lambda$, the ultrasonic absorption per wavelength, on the frequency in aqueous solutions of strontium, barium and zinc acetates (upper figure) and calcium and cadmium acetates (lower figure). Concentration is in moles per litre.

Table IV. Ultrasonic absorption per wavelength in units of 10^{-3} db

Substance	Conc. moles/litre	Frequency (Mc/sec)					
		2.12	6.36	10.61	15.49	19.82	25.80
Zinc Acetate	0.20	70	115	134	116	93	—
	0.10	47	63	70	50	41	98
	0.05	31	30	44	22	17	33
	0.03	24	20	26	14	10	17
Cadmium Acetate	0.6	14.5	26.7	111	136	158	—
	0.4	11.5	24.7	88	108	118	—
	0.2	7.7	17.9	55	69	65	—
	0.1	5.2	11.7	32	43	37	—
	0.05	3.2	7.3	18	22	21	—
Lead Acetate	0.4	0.22	10.4	22	29	34	38
	0.2	0.24	6.1	18	26	29	29
	0.1	0.26	3.6	13	21	24	21
	0.05	0.26	2.2	10	18	21	15

the bivalent acetates. However, no abnormality is observed in the behaviour of the adiabatic compressibility in any of the solutions studied. The compressibility decreases, in all the cases, with the increase of concentration.

(b) *Ultrasonic absorption*: Work on the aqueous solution of mercuric acetate has been abandoned as it is forming a coating on the crystals and the crystal holder. However the measurements made at 2.12 and 6.36 Mc/s on this solution point to a relaxation region below 2 Mc/s. The following features are noticed from a study of the ultrasonic absorption in all the other aqueous acetate solutions.

Two regions of relaxation one below 10 Mc/s and the other above it are noticed in nine out of eleven aqueous acetate solutions. The exceptions are the acetate of lead and cadmium where, probably, the first relaxation is occurring at frequencies far below 2 Mc/s. The second relaxation is observed round about 20 Mc/s in ten acetate solutions. Zinc acetate solution shows a tendency towards a second relaxation beyond the frequency range of this study.

In general, the univalent acetate solutions show lesser absorption than the bivalent acetate solutions.

The first relaxation frequency is about the same for all the acetates of the univalent group (Li, Na, K, NH_4). In the case of the bivalent group (Mg, Ca, Sr, Ba) the relaxation frequency decreases with increasing molecular weight of the salt. Since the second relaxation is occurring at about 20 Mc/s in all the acetate solutions (zinc acetate is an exception) it can be inferred that the cation has no marked influence on the second relaxation frequency as it has on the first.

The maximum value of $\alpha\lambda$ varies as square root of concentration in the univalent acetate solutions in so far as the first relaxation is concerned. The variation of the same for the second relaxation is as cube root of concentration. In bivalent acetate solutions, for both the relaxations, the variation of $(\alpha\lambda)_{\max}$ is as the concentrations. Tamm, Kurtze and Kaiser⁷⁾ have found that $(\alpha\lambda)_{\max}$ varies as concentration for bi-bivalent sulphates.

To see if the hydroxide formed by the hydrolysis of the acetate in water is causing the first relaxation, potassium and barium

hydroxide solutions of concentration 0.2 mole/litre are studied in the entire region of frequencies. No relaxation is observed in either of them. This as well as the various features mentioned earlier eliminate the possibilities such as the excitation of the molecular degrees of freedom, the hydration of the cation etc. as causing the first relaxation. All this leaves a dissociation reaction of the salt into its constituent anion and cation as the possible explanation for the first relaxation observed in the aqueous acetate solutions. Based on this explanation for the first relaxation and using the theory developed by Tabuchi⁸⁾ for ultrasonic propagation in such solutions the authors have calculated various parameters concerning the chemical kinetics of the dissociation reaction. This forms the subject matter of a separate paper to be published elsewhere.

The second relaxation observed in these acetate solutions is strikingly similar to the second relaxation observed by the authors⁹⁾ in the binary mixtures of acetic acid in water. Therefore, this relaxation in the aqueous solutions can be ascribed to the same phenomenon which is causing the second relaxation in the acid water mixtures, namely, the monomer-dimer reaction of the acid. This is because all these acetates in water undergo hydrolysis to some extent and thus form the acid.

The authors thank Professor S. Bhagavantam for his keen interest in this work.

References

- 1) M. Krishnamurthi: Proc. Indan. Acad. Sci. **A41** (1955) 125.
- 2) M. Krishnamurthi and M. Suryanarayana: Curr. Sci. **24** (1955) 369.
- 3) M. Krishnamurthi and M. Suryanarayana: Curr. Sci. **26** (1957) 317.
- 4) P. Bazulin: J. Exp. Theor. Phys. U.S.S.R. **9** (1939) 1147.
- 5) R. E. Barrett, R. T. Beyer and F. L. McNamara: J. Acous. Soc. Amer. **26** (1954) 966.
- 6) C. G. Balachandran: J. Indian Inst. Sci. **38** (1956) 1.
- 7) K. Tamm, G. Kurtze and R. Kaiser: Acustica **4** (1954) 380.
- 8) D. Tabuchi: J. Chem. Phys. **26** (1957) 993.
- 9) M. Krishnamurthi and M. Suryanarayana: J. Phys. Soc. Japan **15** (1960) 349.

Ultrasonic Propagation through Binary Mixtures Containing Acetic Acid

By M. KRISHNAMURTHI* and M. SURYANARAYANA

Physical Laboratories, Osmania University, Hyderabad-7, India

(Received October 1, 1959)

Ultrasonic absorption has been studied by the pulse technique in the binary mixtures of acetic acid in water, methyl and ethyl alcohols and covers a range of 2 to 26 Mc/s. The mixtures are studied from 0 to 100% by weight of the acid. In all the three mixtures, two relaxation processes are observed, the first occurring below the frequency range of the study. The second one occurs near 20 Mc/s in the acid-water mixtures and at much higher frequencies in the other cases. It is qualitatively explained that the monomer-dimer reaction of the acetic acid giving a relaxation near 1 Mc/s has shifted to a higher frequency when mixed in a solvent thus giving rise to a second relaxation in the mixtures.

§ 1. Introduction

The measured ultrasonic absorption in many organic liquids generally exceeds the classical contribution ascribed to viscosity, heat conduction and radiation. This excess absorption is attributed to relaxation effects involving the perturbation by the sound wave of the molecular equilibrium in the liquid. For example, work done by Lamb and Pinkerton¹⁾ from 0.5 to 67 Mc/s and subsequently up to 200 Mc/s by Heasell and Lamb²⁾ revealed a relaxation process in acetic acid round about a frequency of the order of 1 Mc/s depending on temperature. The theory of relaxations in solutions has been developed by Freedman³⁾, who, using his theory, has attributed the relaxation in acetic acid to the perturbation of the monomer-dimer equilibrium of the acid. He further suggested that a study of the binary mixtures of the acid in inert solvents should further help to clarify this issue. This suggestion has been taken up by Piercy and Lamb⁴⁾ who studied the binary mixtures of the acid in some inert solvents like chlorobenzene, nitrobenzene, toluene and *n*-hexane. It is thought desirable by the present authors to study the ultrasonic absorption of the binary mixtures of this acid in water, methyl alcohol and ethyl alcohol. The results of this study are reported in this paper. Even though these solvents are not inert, it is hoped that these results will also be of help in understanding the molecular mechanism causing

the relaxation in the pure acid. A preliminary report of this work has been published elsewhere⁵⁾.

§ 2. Experimental Method

The pulse method of Pellam and Galt with the modification of using two identical quartz crystals, one for transmitting and the other for receiving the ultrasonic pulse, has been adopted in this work. The electronic circuits used from 2 to 10 Mc/s are the same as those described in earlier papers. For a study at higher frequencies in the high absorbing solutions used in this work the input to the transmitting crystals as well as the sensitivity and gain of the receiving amplifiers have to be very much increased. The necessary modifications effected to extend the frequency region up to 30 Mc/s are briefly discussed below.

The transmitting circuit consists of a R.F. oscillator of the Hartley type using a 6 AG7 valve which generates continuous oscillations at any desired frequency between 10 and 30 Mc/s. The output of this oscillator is amplified and simultaneously pulsed by an 807 valve amplifier. By applying positive pulses of 120 volts obtained from the Philips H. F. oscilloscope (G.M. 5660) the amplifier is switched into action, the amplified output being available for the duration of the pulse. Thus the output of this amplifier consists of a series of radio frequency pulses.

At these frequencies it is desirable to have a separate tuned circuit across the transmit-

* Present address: Director's Research Laboratory, Indian Institute of Science, Bangalore, India.

ting crystal and to connect the tuned circuit in the anode load to this combination by a coupling capacity. By this means, the capacity of the crystal and the crystal holder do not form a part of the amplifier circuit. This is an advantage considering the fact that at these frequencies the tuning capacities required are quite small and to maintain the proper L. C. ratio in the anode load all stray capacitances should be reduced to a minimum.

On the receiving side the attenuator is followed by a tuned amplifier covering a frequency range of 12 to 30 Mc/s on the superheterodyne principle. This replaces the wide band amplifier used at the lower frequencies. The intermediate frequency of this amplifier is chosen to be about 10 Mc/s, so that the amplifier may have sufficient band width to retain the pulse shape. The exact I. F. is 10.8 Mc/s and the band width is 100 Kc/s. The gain of the amplifier is of the order of 1000 to 2000, the lower figure being applicable at the higher frequencies.

The ultrasonic velocity is measured at 10.6 Mc/s in the acid-water mixtures only and is accurate to within ± 1 m/sec. The absorption is determined at frequencies 2.12; 6.36; 10.60; 15.47; 19.85 Mc/s in all the three binary mixtures studied. In the case of the acid-water mixtures the measurements are also made at 25.79 Mc/s as the peaks of absorption are observed near that frequency region. The absorption measurements, which are confined to the Fresnel region of the ultrasonic beam, are accurate to within 3 to 6 percent, the lower limit applying to the higher frequen-

cies. All the observations were made at the room temperature of $29^{\circ}\pm 1^{\circ}\text{C}$. The liquids are all fresh standard analytical reagents of guaranteed purity.

§ 3. Results

The observations made on the binary mixtures of the acid with water, methyl alcohol and ethyl alcohol are given in Tables I and II. Table I refers to the values

Table I. Mixtures of acetic acid and water values of $(\alpha\lambda)$ in units of 10^{-3} db

Conc. of Acid wt. per cent of mixture	Frequency (Mc/s)					
	2.12	6.36	10.60	15.47	19.85	25.79
90	156	85	9.5	35	43	51
80	168	98	13	43	46	18
70	144	94	15	50	53	26
60	114	84	18	49	50	32
50	85	61	20	42	42	30
40	60	44	17	30	31	24
30	40	28	12	18	20	15
20	26	13	7.0	9.0	11	8.9
10	12	3.5	2.8	4.4	6.7	6.3
5	4.7	2.4	2.0	3.4	5.0	4.8

of $\alpha\lambda$, the excess absorption per wavelength, at six different frequencies in the range 2 to 26 Mc/s for various concentrations of the acid in the mixture. The excess absorption is obtained after subtracting the value of α/f^2 due to viscosity of the mixture at each concentration from the experimentally determined value of α/f^2 . The viscosity coefficients for various concentrations of the acid in water are taken from the International critical ta-

Table II. Acid-alcohol mixtures values of α/f in units of 10^{-5} db meter⁻¹ sec

Name of Mixture	Conc. of Acid wt. per cent	Frequency (Mc/s)				
		2.12	6.36	10.60	15.49	19.82
Acetic Acid in Methyl Alcohol	80	13.36	6.93	3.82	2.22	3.05
	60	8.48	4.45	2.23	1.13	1.99
	40	4.83	2.58	1.42	0.78	1.34
	20	1.70	1.02	0.74	0.56	0.88
	10	0.53	0.41	0.34	0.47	0.70
Acetic Acid in Ethyl Alcohol	80	21.32	8.40	5.09	3.44	3.47
	60	13.89	6.11	3.29	2.17	2.40
	40	7.00	4.09	2.18	1.47	1.86
	20	3.39	2.23	1.22	0.90	1.23
	10	2.33	1.21	0.80	0.78	1.03

bles (vol. V, p. 20; 1929). The contribution of thermal conductivity and radiation to the absorption has been neglected as it is a small fraction of the viscosity contribution. For the other two binary mixtures, as the velocities are not measured, only values of α/f are given in Table II.

Some of the interesting results are represented graphically in Figures 1 and 2. The velocity is measured in meters/sec and the absorption coefficient $\alpha' = \alpha/f^2$ in 10^{-14} db sec² m⁻¹.

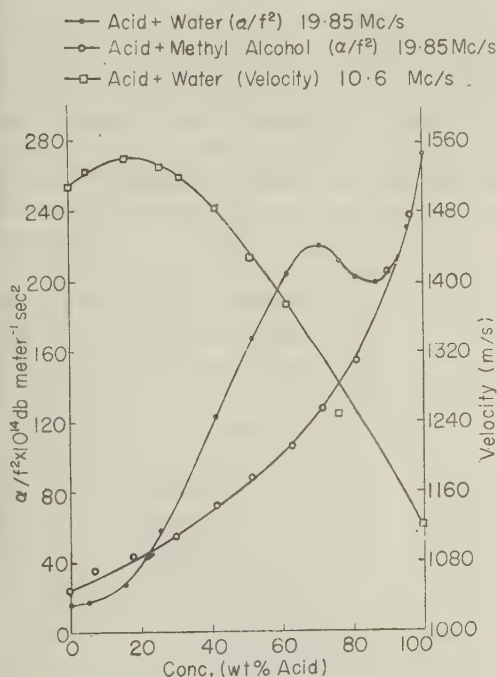


Fig. 1. Ultrasonic absorption coefficient, α/f^2 , at various concentrations of acetic acid in water (●) and in methyl alcohol (○). Ultrasonic velocity in acid-water mixtures (□).

§ 4. Discussion

In each binary mixture, the value of α/f^2 at any concentration of the mixture is different for different frequencies. In the case of the acid-water mixtures, at every frequency of study, interesting peculiarity is observed in the trend of α/f^2 with concentration. Instead of a sagging curve (Figure 1) values of α/f^2 begin to deviate from it from a concentration of 90 per cent by weight of the acid down to very low concentrations. This behaviour can be attributed to a complex formation between the acid and water. Ultrasonic velocity (Fi-

gure 1) also shows deviations near concentrations of 77 and 50 per cent by weight of the acid. These concentrations correspond to the formation of complexes $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ and $\text{CH}_3\text{COOH} \cdot 2\text{H}_2\text{O}$ respectively.

On the other hand, in the case of the alcohol mixtures of the acid, α/f^2 passes smoothly from the value of the acid to that of the respective alcohol (Figure 1). It may be stated that density data (International critical tables vol. III, p. 150; 1929) do not reveal any volume changes in these mixtures. So formation of complexes may not be taking place in these mixtures.

The variation of $\alpha\lambda$, the excess absorption per wavelength, at various concentrations of the acid in water is shown in Figure 2. It is seen from this figure that there are two relaxation regions one below 10 Mc/s and the other above it. The first relaxation occurs much below the lower frequency of this study. In the case of the alcohols, the mixtures only show a tendency towards a second relaxation peak.

The following inferences may be drawn from the f - $\alpha\lambda$ curves of the acid-water mixtures. The second relaxation peak at any given concentration of the mixture is less than the corresponding first relaxation peak. The frequency at which the second relaxation occurs depends on the concentration of the mixture. For higher concentrations of the acid (30 to 80 per cent by weight of the acid) the second relaxation peak is practically constant near 18 Mc/s. At lower concentrations the frequency of peak absorption is increasing with decreasing concentration. This is different from the behaviour of most other relaxing aqueous solutions where the frequency of peak absorption increases with increasing concentration up to a limit.

A qualitative explanation for the second relaxation process may be given. The fact that the second relaxation occurs in all types of solvents studied in this work and in the work of Piercy and Lamb (loc. cit) suggests a common explanation for this relaxation process. As there is no evidence of ionization and complex formation in most of these mixtures these two possibilities are eliminated.

Piercy and Lamb, using the theory proposed by Freedman, have deduced that the second relaxation in the mixtures of the acid in the

inert solvents is due to the perturbation of the monomer-dimer equilibrium. It is, therefore, concluded that the second relaxation observed in the binary mixtures studied in the present work is due to the same reaction. Evidence for such a reaction to exist in the solutions of the acid in water is furnished by Cartwright and Monk⁶⁾. Using conductivity measurements they obtained the equilibrium constant of the monomer-dimer reaction of the acid in water and showed agreement of their value with those obtained by other workers using the distribution and vapour pressure methods. When such a reaction can occur in so active a solvent like water, there is every possibility for this reaction to exist in the binary mixtures of this acid with methyl and ethyl alcohols.

The occurrence of the first relaxation in all the binary liquid mixtures containing the

acid will now be considered. It has already been mentioned that Freedman has ascribed the peak of absorption near 1 Mc/s in the pure acid to the monomer-dimer reaction. Piercy and Lamb ascribe the second relaxation observed in the binary mixtures of the acid in the inert solvents to the same reaction. It is possible that the monomer-dimer reaction which gives rise to a relaxation peak at 1 Mc/s in the pure acid has shifted to about 20 Mc/s in the acid-water mixtures and to higher frequencies for the other binary mixtures of the acid. On an analogy with this it is suggested that the first relaxation occurring in all the binary mixtures might be exhibited by the pure acid at a very much lower frequency than 1 Mc/s. It may be, therefore, useful to investigate the propagation of ultrasonics in the kilocycle region in the pure acid to see if there is a peak in absorption in that frequency range.

The idea of a shift of the relaxation frequency of a pure substance when mixed in a solvent is supported by the results obtained by the authors⁷⁾ in N_2O_4 solutions in water and by the earlier results of Krishnamurthi⁸⁾ in the aqueous solutions of SO_2 . In both the cases, the peaks of absorption for the pure gas are shifted to much higher frequencies when dissolved in water.

In conclusion, the authors thank Professor S. Bhagavantam for his keen interest in this work.

References

- 1) J. Lamb and J. M. M. Pinkerton: *Proc. Roy. Soc. A*, **199** (1949) 114.
- 2) E. L. Heasell and J. Lamb: *Proc. Phys. Soc. London B*, **69** (1956) 869.
- 3) E. Freedman: *J. Chem. Phys.* **21** (1953) 1784.
- 4) J. E. Piercy and J. Lamb: *Trans. Faraday Soc.* **52** (1956) 930.
- 5) M. Krishnamurthi and M. Suryanarayana: *Curr. Sci.* **26** (1957) 317.
- 6) D. R. Cartwright and C. B. Monk: *J. Chem. Soc.* (1955) 2500.
- 7) M. Krishnamurthi and M. Suryanarayana: *Curr. Sci.* **24** (1955) 369.
- 8) M. Krishnamurthi: *Proc. Indian Acad. Sci. A*, **41** (1955) 125.

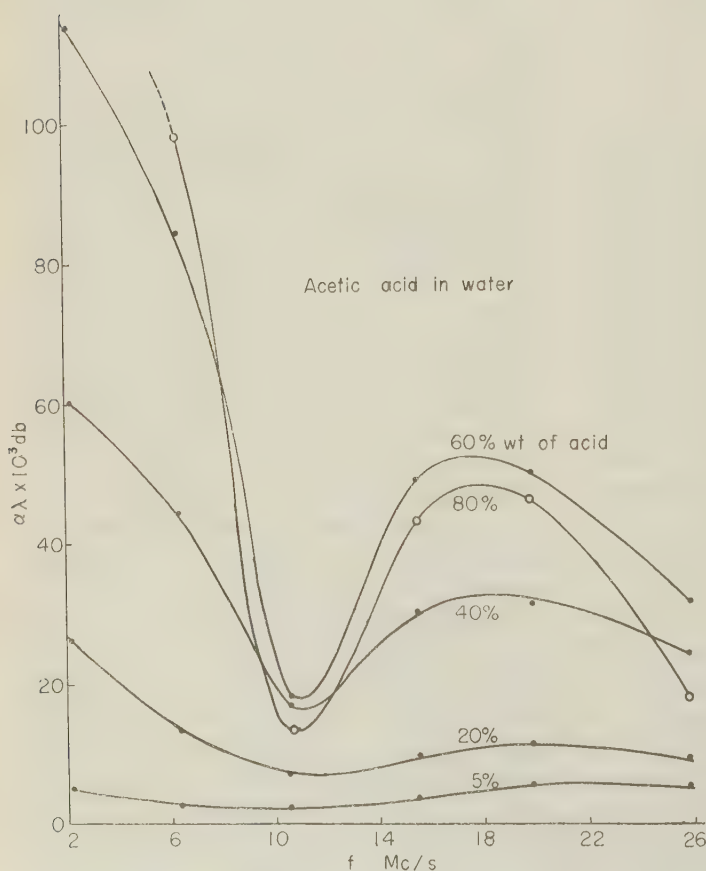


Fig. 2. Dependence of $\alpha\gamma$, the ultrasonic absorption per wavelength, on the frequency in binary mixtures of acetic acid in water for different concentrations of the acid.

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm×7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 353

Photoconductivity in Nickel Doped Germanium

By Yoshitaka FURUKAWA

*The Electrical Communication Laboratory,
Musashinoshi, Tokyo*

(Received November 20, 1959)

The steady state intrinsic photoconductivity in nickel doped high resistivity germanium has been measured at high electric fields upto 10^3 volt/cm to examine the effects of contacts on photoconductivity measurements. Two different contacts, type 1 and 2, were made by soldering indium on etched and ground surfaces of the samples respectively. The typical photocurrent-voltage curves shown in Fig. 1

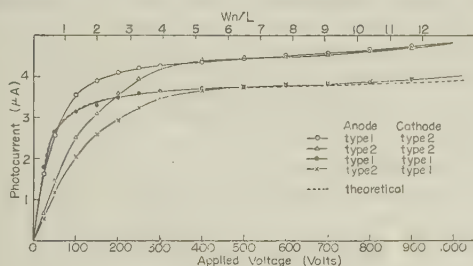


Fig. 1. Photocurrent-voltage curves of *n*-type sample for which $\mu_n = 2.3 \times 10^3$ cm²/volt. sec, $\tau = 5.7$ μ sec at 77°K and $L = 0.9$ cm.

μ_n is the electron mobility, τ is the life time, W_n is the *schurweg* of electrons.

were measured at 77°K under the same light intensity. In each cases, the dark currents were negligibly small as compared with the photocurrents.

It is the unexpected result that the ground layer which gives a low impedance leakage path in usual *p-n* junctions causes large anode drop in both *n*- and *p*-type samples, especially in *n*-type samples, at low temperatures. This may be explained as follows. At low temperatures, the energy bands are bending upwards at the contacts, and the transition regions are extending mainly into the bulk, since the contacts are made of low resistivity *p*-type materials.

When voltages are applied, $V_a, V_c \ll V$ because of the high resistance of the samples at 77°K.

V, V_a, V_c are the applied voltages, voltage drop across the anode barrier, voltage drop across the cathode barrier respectively. The photocurrents can flow only through recombination process with holes supplied from the anode region.

For type 1 anode, holes are injected into the bulk beyond the transition region, and recombination takes place predominantly in the bulk.

In this case, the anode drop is equal to $V_a (\ll V)$. Therefore, the photocurrent-voltage curve fits well to theoretical one¹⁾. For type 2 anode, the ground layer is located at the *p*-side of the transition region, since the layer itself is low resistivity *p*-type. In this case, the recombination takes place predominantly in the layer. Therefore, holes are scarcely injected into the bulk. Electrons arriving at the layer per unit time determine the recombination currents.

When voltages are applied, the potential energy at the layer is lowered by eV_a . However, this lowering effect is expected to be so small that if the concentration of electrons was uniform throughout the bulk, the recombination currents would be much smaller than the photocurrents which would be given by the electric fields $(V - V_a - V_c)/L$, where L is the length of sample, since the layer would be still remaining at the high potential position.

This circumstance differs from that for usual *p-n* junctions in which V_a is larger than that in the present cases because of the low resistivity of the samples.

To equalize the recombination currents with the photocurrents in the interior of the bulk, the mechanism which reduces the electric field in the interior and enhances the number of electrons arriving at the layer per unit time is required.

The local accumulation of free electrons near the anode modifies the form of the transition region in such a way as to lower the potential energy of the layer and enhances the number of elections arriving at the layer.

In addition, the electric fields in the interior are reduced approximately to $(V - V_a - V_c - V_s)/L$.

V_s is the voltage drop across the electron space charge region and occupies fairly large parts of the applied voltages.

In this case, the anode drop is nearly equal to V_s . The barrier height in the *p*-type samples is lower than that in the *n*-type samples (by about a half in thermal equilibrium condition).

This leads to the fact that the anode drop in the *p*-type samples is smaller than that in the *n*-type samples.

Reference

- 1) N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals* (Clarendon, 1957) 122.

J. PHYS. SOC. JAPAN **15** (1960) 354**Fluorine N.S.R. Spectroscopy, II. A "Distant" Carbon-13 Isotope Effect**

By George Van Dyke TIERS

Contribution No. 167 from the Central Research Department, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota, U. S. A.

(Received November 10, 1959)

A nuclear spin resonance (N.S.R.) "isotope effect" upon shielding values for fluorine atoms attached to C^{13} has recently been discovered¹⁾. In each case the heavy isotope produced a band displacement of 0.1 to 0.2 parts-per-million in the direction of greater shielding.

Although spin-spin interaction was observed in the system $F-C^{12}-C^{13}$, no isotopic shift was detected¹⁾. As both the sign and the magnitude of such a C^{13} effect might be theoretically interpretable, particular attention has been given to precision measurement in the present work.

The purity of the compounds studied was excellent, no spurious bands being found in the N.S.R. spectra. The $CF_2=CCl_2$ was obtained from the General Chemical Co., the $CFCl=CCl_2$ from the Columbia Organic Chemical Co. (Columbia, South Carolina, U.S.A.), while the CF_3CO_2H and the CF_3CCl_3 were synthesized in our laboratories. The C^{13} isotopic isomers were present at their natural abundances. The undiluted compounds were employed for the C^{13} studies. For the measurement of the following ϕ^* -values²⁾, dilute solutions in CCl_3F were used; $CF_2=CCl_2$, $+88.54 \pm 0.01$ (3%); $CFCl=CCl_2$, $+79.33 \pm 0.01$ (10%); CF_3CO_2H , $+76.542 \pm 0.005$ (5%)³⁾; and CF_3CCl_3 , $+82.209 \pm 0.002$ (3%)²⁾.

The N.S.R. spectrometer and the measurement techniques used have been described in great detail^{3),4)} the latter having been developed for the detection of the exceedingly small $C^{13}H$ isotope effect⁴⁾. The results, presented in Table I, are in each case the averaged values from 6 to 8 separate measurements.

Table I. The Excess Fluorine N.S.R. Shielding, $\Delta\phi$, Produced by Distant C^{13} in Two-Carbon Compounds.

Compound	$\Delta\phi$, p.p.m. ^a ($F-C^{12}-C^{13}$)	J, c/s ^a ($F-C^{12}-C^{13}$)	$\Delta\phi$, p.p.m. ^b ($F-C^{13}$)	J, c/s ^b ($F-C^{13}$)
CF_3CCl_3	+0.014	43.1	+0.131	282.5
CF_3CO_2H	+0.021	44.1	+0.129	283.2
$CF_2=CCl_2$	+0.030	44.2	+0.103	288.9
$CFCl=CCl_2$	+0.032	43.7	+0.112	303.1

(a) Standard deviations of the averaged values are ± 0.002 p.p.m. and ± 0.10 c/s for CF_3CCl_3 and

CF_3CO_2H , and ± 0.003 p.p.m. and ± 0.20 c/s for the olefins.

(b) Standard deviations of the averaged values are ± 0.002 p.p.m. and ± 0.13 c/s. These values are quoted from Ref. 1 for purposes of comparison.

The small excess shielding produced by "distant" C^{13} is shown to vary by a statistically significant factor of two among the compounds of Table I. No correlation is observed between this strongly varying quantity and the presumably closely related other measurements listed in Table I, nor to the fluorine shielding values, $\phi^{*2)$, listed for the compounds. A new influence apparently must be sought. A tentative suggestion (which cannot at present be verified) has to do with the structure of carbon atoms in the valence-bond system concerned. The magnitude of the C^{13} effect increases with the number of trigonal carbons in the $F-C-C^{13}$ system; this "correlation" may perhaps extend (with the opposite sign!) to the smaller $F-C^{13}$ system. Gutowsky has offered an explanation of isotope effects in the systems $H-C^{12}-D$ and $F-C^{12}-D$, based on a simple electrostatic model⁵⁾ which if extended to the $F-C^{12}-C^{13}$ case would appear to imply a relatively large amplitude for the in-plane $F-C=C$ bending vibration of the fluorinated olefins.

It is of particular theoretical interest that the "distant" spin-coupling constant, $J(F-C^{12}-C^{13})$ appears virtually invariant in the compounds of Table I. One might have expected the opposite result, in view of the very large variations in structure. Experiments are currently under way to determine the relative sign of the two C^{13} coupling constants.

I am particularly indebted to P. C. Lauterbur of the Mellon Institute for the privately-communicated results of Ref. 1, without which it is probable that the present work would not have been begun. I thank Professor H. S. Gutowsky of the University of Illinois for a pre-publication copy of Ref. 5. Donald Hotchkiss is responsible for the careful maintenance and operation of our N.S.R. equipment.

References

- 1) P. C. Lauterbur (paper in course of preparation).
- 2) G. Filipovich and G. V. D. Tiers: J. Phys. Chem. **63** (1959) 761.
- 3) G. V. D. Tiers: J. Phys. Chem. **62** (1958) 1151.
- 4) G. V. D. Tiers: J. Phys. Chem., in press.
- 5) H. S. Gutowsky: J. Chem. Phys., in press.

J. PHYS. SOC. JAPAN **15** (1960) 355

Nuclear Quadrupole Resonance of Nitrogen in Cyanuryl Chloride

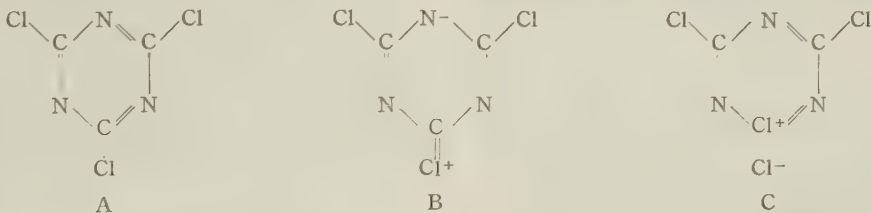
By Shoji KOJIMA and Midori MINEMATSU
Department of Physics, Tokyo University of Education, Otsuka, Tokyo

(Received November 6, 1959)

The quadrupole resonance of N¹⁴ in solid cyanuryl chloride has been studied by using a Pound-Watkins type recording spectrometer with Zeeman modulation¹⁾. The rate of frequency sweep of the spectrometer was about 4.5 kc per minute and the power of level was about 0.5 volts. When the spectrometer was swept from high to low frequency, a resonance line was detected at the frequency of 3.0445±0.0004 Mc, and when the direction of frequency sweep was reversed, another line was observed at the frequency of 3.0799±0.0004 Mc. These frequencies were measured for a solidified sample of about 8 cc at liquid nitrogen temperature. In these experiments where a Zeeman modulation field of about 20 gauss was used, negative wings of the absorption line were scarcely observed on all traces.

When the Zeeman field was reduced to 10 gauss, the two lines having special shapes were observed at every sweep, although the signal to noise ratio decreased. For the frequency sweep from low to high the shape of the low frequency line was a simple negative wing without main absorption part and that of the high frequency line was a usual absorption type but lacking a negative wing. For the frequency sweep from high to low the situation was reversed. Such shapes of the traces could be explained through a saturation effect¹⁾. The phenomenon of missing of one of the lines at each sweep under the Zeeman modulation field of 20 gauss seems to be caused by smearing up the negative wing. Therefore, the two lines are accounted for the splitted pair due to a finite asymmetry parameter. The measured frequencies of lines give the quadrupole coupling constant of 4.083 Mc and the asymmetry parameter of 1.7%. The smallness of the asymmetry parameter is verified by the fact that the lines could be detected with the small Zeeman field¹⁾.

The structure of cyanuryl chloride is usually understood to consist of the following three types of valence-bond structures^{2),3)}. The electron distribu-



tions in the structures A and C give no asymmetric field gradient for the nitrogen nucleus. The structure B alone contributes to the finite asymmetry parameter. Assuming that the bonds of nitrogen are sp²-hybrid with 1/3 s character and not taking into account for the ionic character of the bonds, the asymmetry parameter of field gradient tensor, η , is expressed by

$$\eta = \frac{9}{4} \frac{f}{1+c},$$

where f is the fractional importance of the structure B and c is the screening constant which is known for nitrogen to be about 0.32⁴⁾. Putting $\eta=1.7\%$ the equation gives $f=1.0\%$.

Morino et al²⁾ and Adrian³⁾ studied the fractional importance of the structure B through the double bond character of the carbon-chlorine bond which was determined from the nuclear quadrupole resonance of Cl³⁵. According to their analysis f is 10% or 8.5%, which is reasonable to account for the length of carbon-chloride bond⁵⁾. In order to search for the nitrogen lines corresponding to the large asymmetry parameter, the spectrometer was run in the frequency range between 2.5 Mc and 3.5

Mc. But any new line was not found. In view of the experiment on chlorine showing a single resonance it seems possible that the observed lines are the only pair. Thus the small asymmetry parameter of nitrogen resonance is also certain. The difference in asymmetry parameter between chlorine and nitrogen will be presumably accounted for if the negative charge is not localized at the nitrogen atom in the model of valence bond structure of B.

References

- 1) M. Minematsu: J. Phys. Soc. Japan **14** (1959) 1030.
- 2) Y. Morino, T. Chiba, T. Shimozaawa and M. Toyama: J. Phys. Soc. Japan **13** (1958) 869.
- 3) F. J. Adrian: J. Chem. Phys. **29** (1958) 1381.
- 4) B. P. Dailey and C. H. Townes: J. Chem. Phys. **23** (1955) 118.
- 5) Y. Akimoto: Bull. Chem. Soc. Japan **28** (1955) 1.

J. PHYS. SOC. JAPAN 15 (1960) 356

On the X-Ray Temperature Diffuse Scattering of Anthracene and Stearic Acid

By Shoichi ANNAKA* and J. L. AMORÓS

*Departamento de Cristalografía.
C. S. de I. C. Madrid*

(Received December 7, 1959)

The X-ray diffuse scattering of anthracene, $C_{14}H_{10}$, was studied qualitatively in the greater part of the reciprocal space by the systematic Laue method. Specially interesting areas were also studied quantitatively by a counter method. The diffuse scattering was composed of sharp streaks, thin planes and continuous regions. The strong diffuse scattering in some places where the structure factor is zero, shows that the independent vibrations of the molecules must be taken into account besides

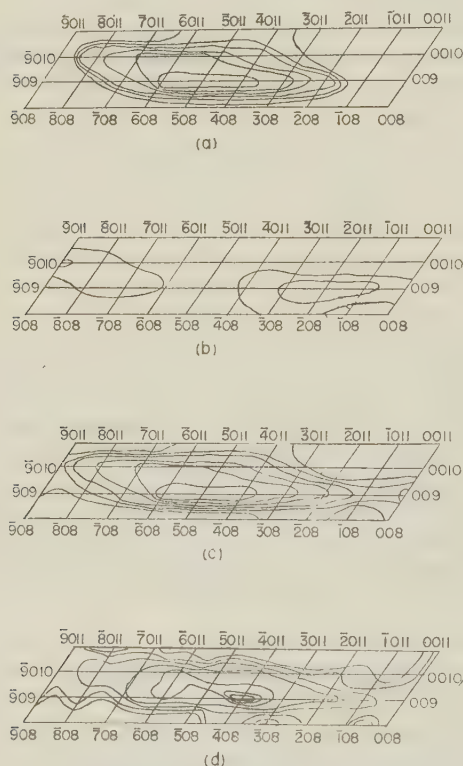


Fig. 1. Intensity of diffuse scattering of anthracene. (a) Theoretical isodiffusion lines (independent harmonic vibration). (b) Theoretical isodiffusion lines (independent libration). (c) harmonic vibration and independent libration). (d) Experimental isodiffusion lines.

* On temporary leave from Tokyo University of Education, Tokyo.

the normal thermal waves. This is the direct consequence of the fact that the molecules of anthracene are connected by the weak van der Waals forces. Furthermore the analysis of Raman spectrum and crystal structure shows that the molecules are rotationally oscillating about the three orthogonal axes.

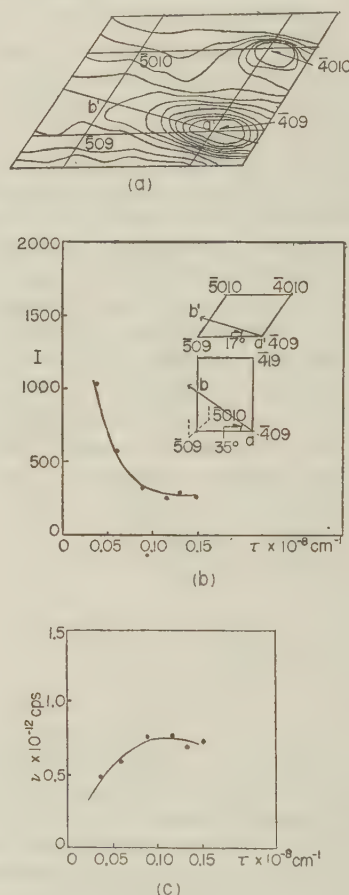


Fig. 2. Intensity of diffuse scattering of anthracene. (a) Experimental isodiffusion line. (b) Intensity change along the line ab. The intensity scale corresponds to that when the intensity of the Compton scattering from the same crystal is 70 at the deflection angle $\varphi=120^\circ$. (c) Approximate dispersion curve for the transverse wave along the line ab.

On the basis of these facts, we calculated the diffuse scattering by using the models of the independent motions of molecules, which were composed of harmonic vibration and libration.

The experimental intensity distribution of diffuse regions of anthracene is explained approximately by the independent harmonic vibration except near the a^* -axis. This agrees with the work of Charlesby, Finch and Wilman¹⁾. The accurate quantitative data of the diffuse regions obtained by

a diffractometer is explained when both harmonic vibration and libration (oscillation amplitude $\approx 6^\circ$ about N -axis) are taken into account. The result is shown in Fig. 1 in which the contours of the intensity from a unit cell are given (the contour lines correspond to 25, 50, 100, 200 etc. in electron units).

A section of a sharp plane of diffuse scattering associated with $(\bar{4}09)$ is shown in Fig. 2, a. The plane $(\bar{4}09)$ is approximately perpendicular to the planes of molecules. The intensity change along the line ab in this plane was measured (Fig. 2, b) We have calculated the dispersion curve (Fig. 2, c) for the transverse waves in the perpendicular direction to the planes of molecules. From this curve an approximate force constant ($\beta = 1.6 \times 10$ dyne/cm) has been calculated for the transverse motion of the molecules in the above said direction. A simple chain model and a pseudo unit cell were used in these calculations.

The diffuse scattering of stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, was also studied by the systematic Laue method. The intensity distribution of such diffuse scattering was also explained qualitatively by the independent harmonic vibration.

The detail of this note will be reported elsewhere. The present work has been sponsored in part by the Directorate of Solid-State Science, Air Force Office of Scientific Research, through the European Office A. R. D. C. One of us (S. A.) is indebted to the Departamento de Cristalografía, C. S. de I. C. Madrid for receiving a grant during his work in Spain.

Reference

- 1) A. Charlesby, G. L. Finch and H. Wilman: Proc. Phys. Soc. London **51** (1939) 479.

J. PHYS. SOC. JAPAN **15** (1960) 357

Photoconductivity of Cd-ZnS Mixed Crystal

By Makoto KIKUCHI and Sigeru IIZIMA

*Electrotechnical Laboratory,
Tokyo, Japan*

(Received December 11, 1956)

Relatively large bulky single crystals of Cd-ZnS are prepared by a method which is similar to Reynolds-Czyzak method^{1,2}). Luminescent pure powder of CdS and ZnS is mixed and sealed in vacuum in fused quartz ampoules, then heated at 1250°C for 72 hours.

We obtain the disks which consist of several single crystals bounded by grain boundaries by this method. On the pieces cleaved from these crystals

evaporated indium electrodes are deposited properly. Spectral sensitivity of photocurrents at 1 volt bias is measured. Monochromatic light is obtained by using Hitachi Photo-Electric Spectro-photometer. The results are shown in Fig. 1. Corrections for

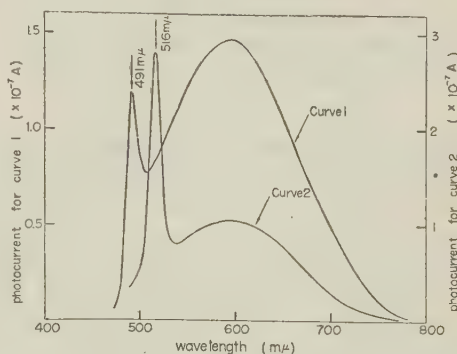


Fig. 1. Photocurrent *vs* wavelength of mixed crystal and pure crystal.

the dispersion of the prism and the energy distribution of the tungsten lamp used as a light source are not done. Curve 1 is obtained from the sample cleaved from the crystal which is made of 26.5 gram CdS powder and 4.0 gram ZnS powder. For comparison, curve 2 obtained from the sample pure CdS crystal prepared by the same method is shown in the figure. As is seen in the figure, the peak of photocurrent corresponding to the absorption edge is shifted to shorter wavelength, when ZnS powder is added to CdS.

In addition to these sharp peaks, another peak at about $600\text{ m}\mu$ appears. This peak is probably due to the presence of oxygen that has been absorbed in the powder or the ampoule.

In this experiment, we can show that the band gap of sulphide crystal may be varied continuously and arbitrarily by adding ZnS to CdS.

Investigation of the other properties of the mixed crystal is in progress and will be published in the near future.

References

- 1) R. Czyzak et al.: J. Appl. Phys. **23** (1952) 932.
- 2) M. Kikuchi and S. Iizima: J. Phys. Soc. Japan **14** (1959) 1638.

J. PHYS. SOC. JAPAN **15** (1960) 358

Fine Structure in the $N^{14}(\gamma, n)N^{13}$ Activation Curve II

By Naoshi MUTSURO, Kazuo SATO
and Masanori MISHINA

Department of Physics, Tohoku University
Sendai, Japan

(Received December 16, 1959)

In the previous note¹⁾ the activation curve of the $N^{14}(\gamma, n)N^{13}$ reaction in the energy region 11~17 MeV was reported, and eight breaks were observed in this energy region.

Recently we extended the activation curve to the higher energy region, from 14.70 to 19.50 MeV, and three new breaks at the energies of 16.35, 18.05 and 19.10 MeV were observed.

The experimental procedures are the same as the previous one¹⁾, and the activation curve is shown in Fig. 1, in which the yields per unit monitor

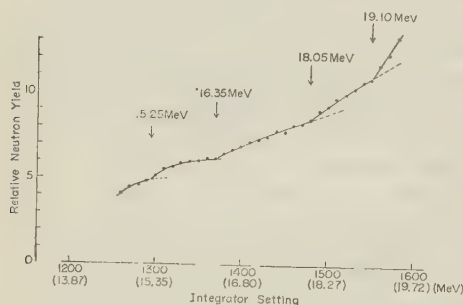


Fig. 1. Activation Curve of $N^{14}(\gamma, n)N^{13}$ above 14.70 MeV.

response are plotted as a function of the maximum energy E_m of the bremsstrahlung spectrum. Breaks are clearly seen at the energies of 16.35, 18.05 and 19.10 MeV.

Assuming that all resonances have the same resonance width, relative cross sections corresponding to these breaks are shown in Fig. 2. The resonances below 14.70 MeV are taken from the activation curve of the previous work¹⁾. The errors of these cross section values are about 10 percent

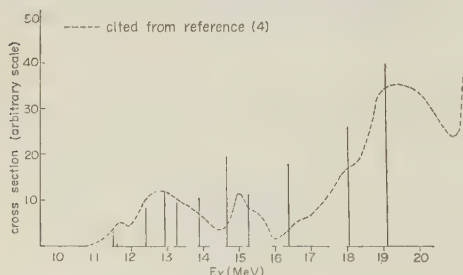


Fig. 2. Cross Section of $N^{14}(\gamma, n)N^{13}$.

or larger, because these values are deduced from the comparison of the linear extrapolations of scallops of these breaks. The cross section curve can be deduced directly from the activation curve by photon difference method²⁾ or by inverted matrix method³⁾ of Penfold and Leiss, but the resultant cross section curve depends sensitively on smoothed condition of the activation curve, and the shapes and energies of the resonances cannot be obtained very precisely, so we did not take this method.

In the Fig. 2 the dotted line is taken from King⁴⁾ et al. Present data do not seem to be inconsistent with the gross resonances obtained by King⁴⁾ et al, for instance, two resonances at the energies of 11.49 and 11.61 MeV correspond to the gross resonance at 11.5 MeV and resonances at 12.39, 12.92, 13.28 and 13.87 MeV correspond to the gross resonance at 13.2 MeV. Resonances at 14.62 and 15.25 MeV correspond to the gross resonance at 15.2 MeV. Thus we conclude that the gross resonances obtained by King⁴⁾ et al may correspond to the group of comparatively sharp resonances observed by us.

King⁴⁾ et al. considered that the resonance at 13.25 MeV corresponded to the single particle resonance predicted by Fujii⁵⁾, but their integrated cross section from threshold to 16 MeV was 1.8 MeV-mb, which is much smaller than the value of 13.5 MeV-mb predicted by Fujii⁵⁾.

The breaks at the energies of 16.35, 18.05 and 19.10 MeV correspond to the newly observed compound states of N^{14} , and these states may have odd parity, and possible spins of these states are 0, 1 or 2, because the spin of the ground state of N^{14} is 1^+ , and usually the photodisintegration in this energy region proceeds through an electric dipole transition.

The authors are indebted to Mr. T. Inoue for his assistance in much of the experimental work.

References

- 1) N. Mutsuro, Y. Ohnuki, K. Sato, K. Kageyama and M. Kimura: J. Phys. Soc. Japan **14** (1959) 1557.
- 2) L. Katz, A. G. W. Cameron: Canad. J. Phys. **29** (1951) 518.
- 3) A. S. Penfold, J. E. Leiss: Analysis of Photo Cross Section; May (1951).
- 4) J. D. King, R. N. H. Haslam, R. W. Parsons: Canad. J. Phys. (to be published)
- 5) S. Fujii: Progr. Theor. Phys. **21** (1959) 511.

J. PHYS. SOC. JAPAN 15 (1960) 359

Thickness Dependence of Domain Orientation in Thin Nickel Films

By Kaizo KUWAHARA and Mitita GOTO
Department of Physics, Faculty of Science,
Hiroshima University

(Received December 18, 1959)

Kittel¹⁾ theoretically predicted that, in ferromagnetic films, the domain configuration strongly depends on the thickness. The present preliminary paper is devoted to make this clear by measuring the magnetoresistance effect of Ni films.

The specimens were prepared by evaporating Ni on microscope slide glasses maintained at room temperature and then coating with SiO₂ film²⁾. The magnetoresistance ($\Delta R/R$) was measured by an ordinary d.c. method. Fig. 1 shows the result

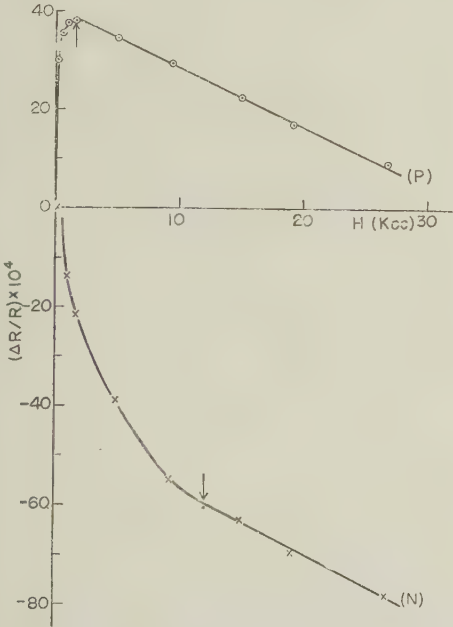


Fig. 1. $\Delta R/R$ in the specimen of 500 Å.

obtained on the annealed specimen of 500 Å thick, as an example. The notations of P and N signify the measurements when the applied fields are parallel to the d.c. current and normal to the film plane, respectively. The rapid increase (P) or decrease (N) in low fields is almost due to the reorientation of domains. The linear decrease in high fields is principally due to the increase in intrinsic magnetization. Then the fields enough to saturate the magnetization technically, H_s , are easily estimated; these are shown with arrows in the figure.

H_s obtained is plotted against film thickness in Fig. 2, where A and B show the results after and

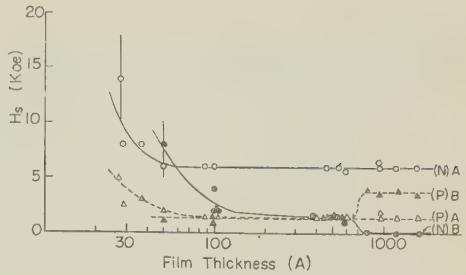


Fig. 2. H_s vs film thickness. Preferable domain orientation changes from parallel to normal at about 700 Å.

before annealing (400°C-10h), respectively. In the estimation of H_s for N, the demagnetizing field, $4\pi M_s$ (≈ 6 Kc), is corrected.

In the case of B, it may be recognized that an easier magnetization direction seems to change from parallel to normal to the film plane at about 700 Å; the domains may orient preferably parallel and normal to the film plane below and above that thickness, respectively. According to Kittel¹⁾, such a critical thickness d_c is expressed as

$$d_c = 6.8 M_s^2 \cdot \sigma / K^2 .$$

In the present case, the magnetocrystalline anisotropy energy K is not effective because the specimen is composed of microcrystals oriented at random. However, the magnetoelastic anisotropy energy, caused by the isotropic inner tensile stress T and the isotropic negative magnetostriction constant λ , is expected to play the roll of K . Then $K \approx (3/2) \lambda T$. Using 8×10^9 dyne/cm² for T ³⁾, -4×10^{-5} for λ , 5×10^3 for M_s and 1 erg/cm² for σ , we obtain $d_c \approx 700$ Å. This is surprisingly consistent with that obtained in the present experiment.

In the case of A, the preferred domain orientation seems to lie always in the film plane. This may be due to partial release of the inner stress by the annealing.

In both cases of A and B, H_s appears to rise abnormally as the thickness extremely decreases. This behavior would be explained as the strong restraint of local magnetization at the interface between the bottom of film and the surface of substrate, but more detailed study should be required.

The authors wish to represent sincere thanks to Prof. E. Tatsumoto for his helpful discussions.

References

- 1) C. Kittel: Phys. Rev. **70** (1946) 965.
- 2) K. Kuwahara: J. Phys. Soc. Japan **14** (1959) 1247.
- 3) R. W. Hoffman: Proc. Phys. Soc. London **B**, **67** (1954) 497.

J. PHYS. SOC. JAPAN **15** (1960) 360~361**Magnetic and Electrical Anomalies of Iron Telluride Single Crystals**By Rokuroh NAYA, Miyuki MURAKAMI
and Eiji HIRAHARA*Department of Physics, Faculty of Science,
Tohoku University, Sendai*

(Received December 28, 1959)

The magnetic properties of iron telluride have been studied by several workers¹⁾, and the electrical properties have been also studied by Finlayson et al.²⁾ with single crystals. An anomaly which no previous workers have reported has been observed in our laboratory by the sample of stoichiometric composition and of tellurium-less compositions.

All specimens studied in this work are single crystals prepared by Bridgmann's method. The specimens of stoichiometric composition and of tellurium-less compositions have a sharp cleavage, and the samples of tellurium-excess compositions, have no remarkable cleavage.

The magnetic behaviors of the samples of tellurium-rich composition $\text{FeTe}_{1.10} \sim \text{FeTe}_{1.15}$ are similar to those reported by the previous workers as shown in Fig. 1 in which for the sake of simplicity

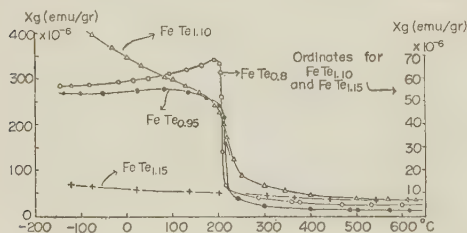


Fig. 1. Temperature dependences of the susceptibility for $\text{FeTe}_{0.8}$, $\text{FeTe}_{0.95}$, $\text{FeTe}_{1.10}$ and $\text{FeTe}_{1.15}$. The ordinate indicated on the right hand side is for $\text{FeTe}_{1.10}$ and $\text{FeTe}_{1.15}$.

the behaviors of $\text{FeTe}_{1.10}$ and $\text{FeTe}_{1.15}$ are only shown. It is noticed the sample of stoichiometric shows a large value of susceptibility below 260°C, and seems to behave as ferromagnetic or ferrimagnetic. The samples of tellurium-less composition show a sharp anomaly at the temperature 206°C which is lower than that of the stoichiometric. The anomaly becomes steeper when the content of tellurium increases, as seen in Fig. 1.

The magnetization was measured for $\text{FeTe}_{0.8}$ in various external field from 1.3 kilo-oersteds up to 6.0 kilo-oersteds as shown in Fig. 2.

An anisotropy of the susceptibility observed when the external magnetic field was applied in perpendicular to and in parallel with the cleavage surface of the sample $\text{FeTe}_{0.8}$ came to be about 15% at the room temperature.

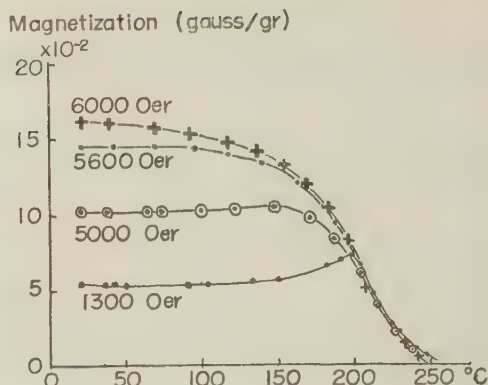


Fig. 2. Magnetization curves for $\text{FeTe}_{0.8}$.

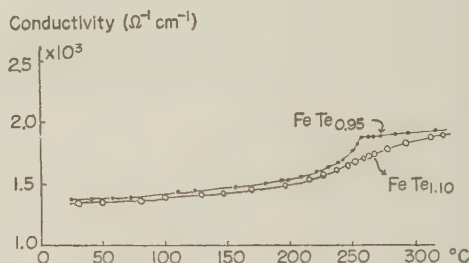


Fig. 3. Temperature dependences of the conductivity for $\text{FeTe}_{0.95}$ and $\text{FeTe}_{1.10}$.

On the electrical conductivity, only two results measured for $\text{FeTe}_{0.95}$ and $\text{FeTe}_{1.10}$ are shown in Fig. 3. In the former case a well defined anomaly is observed at 260°C.

The anomalies mentioned above may be interpreted in the following way. It will be unreasonable that the magnetization of the samples with tellurium-less composition is due to excess iron because the Curie temperatures of iron and its compound (probably its oxide) are far higher than the temperature at which our anomaly occurs. The sample with tellurium-less composition may be considered a link composition between the tetragonal FeTe (the B 10 type) and the tetragonal Fe_2Te (the C 38 type). Therefore, some positions of the sites $(0, \frac{1}{2}, z)$ and $(\frac{1}{2}, 0, \bar{z})$ of the tetragonal FeTe may be occupied by the excess iron atoms, and some ordering orientation of these excess iron atoms will present the ferromagnetism or the ferrimagnetism below the temperature at which the anomaly was observed and above the temperature the ordering will be scattered by the thermal energy of lattice.

Grønvald et al.³⁾ have also reported that the tellurium-less composition $\text{FeTe}_{0.90}$ was a link composition between FeTe and Fe_2Te by the X-ray investigation. In our laboratory the anomaly is now being investigated by means of the X-ray diffraction.

This work was supported by the Scientific Re-

search Expenditure of the Ministry of Education.

References

- 1) S. Chiba: J. Phys. Soc. Japan **10** (1955) 837.
H. Kondoh and E. Uchida: J. Phys. Soc. Japan **10** (1955) 357. I. Tsubokawa and S. Chiba: J. Phys. Soc. Japan **14** (1959) 1120.
- 2) D. M. Finlayson, D. Greig, J. P. Llewellyn and T. Smith: Proc. Phys. Soc. London **B**, **69** (1956) 860.
- 3) F. Grønqvold, H. Haraldsen and J. Vihovde: Acta Chem. Scand. **8** (1954) 1927.

J. PHYS. SOC. JAPAN **15** (1960) 361~362

Differential Cross Sections for the $N^{14}(d, p)N^{15}$ Ground State Reaction at the Deuteron Energy of 16 MeV

By Susumu MORITA, Nawoyuki KAWAI,
Naoyuki TAKANO, Yorio GOTÔ,
Reiko HANADA,

Department of Physics, Kyushu
University, Fukuoka

Yutaka NAKAJIMA,

Department of Physics, University of
Tokyo, Tokyo

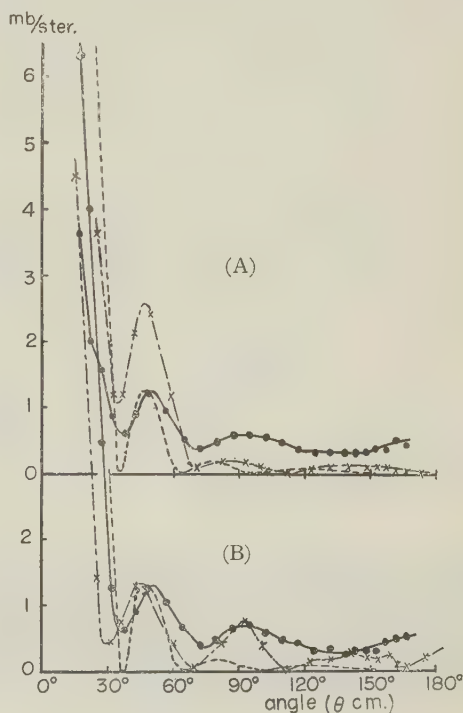
Shigeo TAKEMOTO and Yûki YAEHASHI

Department of Physics, Tohoku
University, Sendai

(Received December 16, 1959)

This is a report of the preliminary experiment on the measurements of the change of angular distributions with deuteron energy in the $N^{14}(d, p)N^{15}$ ground state reaction. A collimated beam of 16.2- and 16.7-MeV deuteron from cyclotron was incident upon a gas target placed at the center of the scattering chamber. The scattering chamber and the detector system used have been described elsewhere¹⁾. Nitrogen gas of 41.8 cmHg pressure was contained in the target cell of brass cylinder of 9 cm diameter. The cell windows, through which the deuteron beam and outgoing proton passed, consisted of 0.02 mm thick aluminium foils cemented with Epikote resins on the cylindrical surface of the target cell. The target volume viewed by the scintillation counters was defined by two rectangular slits of $5 \times 12 \text{ mm}^2$ for the forward counter and of $5 \times 15 \text{ mm}^2$ for the backward counter. The scattered deuterons and alpha particles produced by any reactions, were eliminated by 1 mm thick aluminium absorber, placed just before the scintillators and the protons were detected with 2 mm

thick CsI(Tl) crystals, which were thick enough to stop all the protons. The counts were obtained at the opposite directions to the target, simultaneously with the two sets of scintillation counters. Through a long rectangular slit system, the protons entered the monitor counter placed at the direction of 55° and outside the scattering chamber. Only the proton group to the ground state of N^{15} was selected by the discriminator bias. The angular distributions obtained are shown in Fig. 1, together with the theoretical stripping curves. Warburton and McGruer²⁾ measured the angular distribution in the forward directions with deuteron of 14.8 MeV



- (A) ●; Present result
 $N^{14}(d, p)N^{15}$, $E_d=16.7 \text{ MeV}$
 $E_x=35.3 \text{ MeV}$
×; Nonaka et al.
 $C^{12}(\alpha, p)N^{15}$, $E_\alpha=38.6 \text{ MeV}$
 $E_x=36.1 \text{ MeV}$
---; Stripping theory
- (B) ●; Present result
 $N^{14}(d, p)N^{15}$, $E_d=16.2 \text{ MeV}$
 $E_x=34.9 \text{ MeV}$
×; Nonaka et al.
 $C^{12}(\alpha, p)N^{15}$, $E_\alpha=37.1 \text{ MeV}$
 $E_x=35.0 \text{ MeV}$
---; Stripping theory

Fig. 1. Angular distributions of protons. E_x , in the figure, is the excitation energy of compound nucleus O^{16} .

and obtained agreement with Butler's stripping formula with $r_0 = 5.5 \times 10^{-13}$ cm. The present results are best fitted to Bhatia's formula with $r_0 = 7.0 \times 10^{-13}$ cm. The absolute values of the cross sections may have errors of about 20%.

The present angular distributions were compared with those for the $C^{12}(\alpha, p)N^{15}$ reaction, obtained by Nonaka et al.¹⁾, with the energies of alpha particles corresponding to nearly the same excitation energies of the compound nucleus O^{16} as those for the present $N^{14}(d, p)N^{15}$ reaction. It seems to be that the angular distributions in both reactions resemble each other in some points. This may be only a chance coincidence. But, although the angular distributions of both reactions in the forward directions are explained by the stripping theory, the cross sections in the angular range near 90° and in backward directions may be due to the compound nucleus formation. This work will be continued to more extensive range of deuteron energy.

This work was preformed with the variable energy cyclotron of the Institute for Nuclear Study, the University of Tokyo. The authors express their cordial thanks to Prof. Nonaka and the cyclotron crew of INS.

References

- 1) I. Nonaka et al.: J. of Phys. Soc. Japan **14** (1955) 1260. S. Morita et al.: To be published in the J. Phys. Soc. Japan.
- 2) E. K. Warburton and J. N. McGruer: Phys. Rev. **105** (1957) 639.

J. PHYS. SOC. JAPAN **15** (1960) 362~363

A Curious Characteristic of P-N-P-N Junctions

By Takao KURATA and Kiichi KOMATSUBARA*

Semiconductor Engineering Division,
Kobe Kogyo Corporation

(Received November 19, 1959)

The P-N-P-N junction used in the present investigation is fabricated with thin diffused N-layers on both sides of a P-type silicon wafer, and alloyed P-layer on one side of the diffused N-surfaces,

When these samples were cooled, the forward voltage-current characteristics showed a curious behavior as shown in Fig. 1.

At the temperature about 20°C or below, one valley point appeared at negative resistance region, and V-I curves at the region A of this valley (Fig. 1) were relatively temperature insensitive.

* Now, it is not present adress.

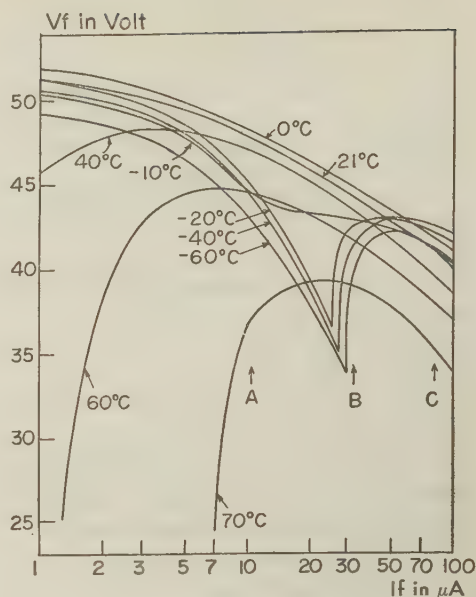


Fig. 1. The forward V-I characteristics at different temperatures; small current region.

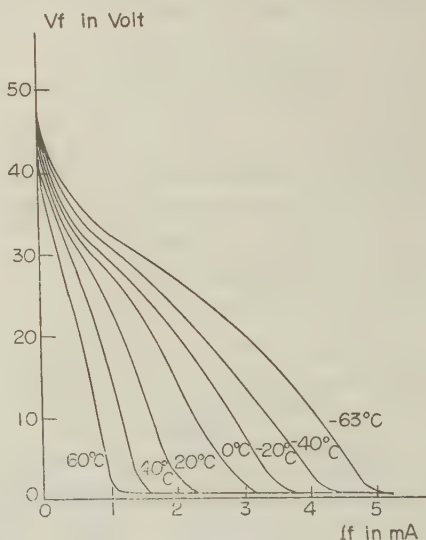
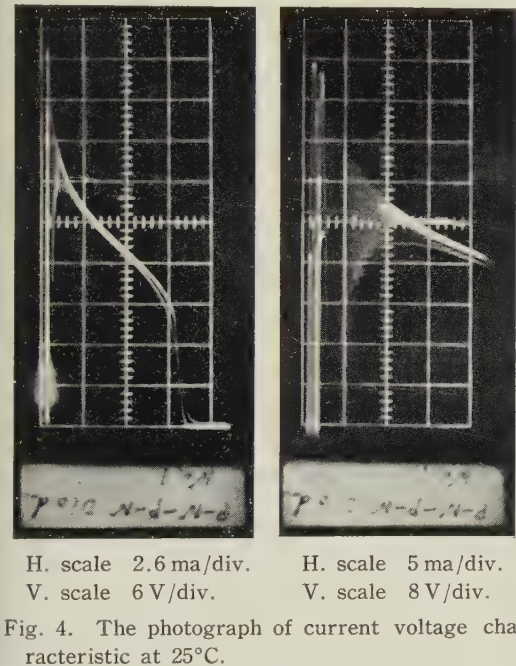
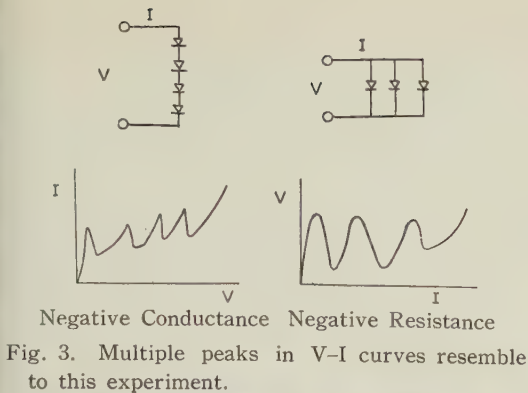


Fig. 2. The forward V-I characteristics. If in mA at different temperatures; large current region.

The increasing of voltage over the valley point was very steep and the current value of this steep region B was increased as the temperature was decreased. The region C is well known characteristics caused by avalanche multiplication, and the temperature dependency of this region is shown in Fig. 2.

To explain this phenomenon, further investigation is necessary. If one connects the semiconductor devices with negative conductance in series or negative resistance in parallel as shown in Fig. 3D,



it is seen that some multiple peak points appear in V-I curves. In the case of this P-N-P-N junction, therefore, something of double mechanisms to produce negative resistance may be thought of.

In region A, some oscillational phenomena were observed as shown in Fig. 4. In this measurement a constant pulse current of small repetition rate was used to preclude thermal effects.

Reference

- 1) Z. Kitamura and S. Mizutani: private communication.

J. PHYS. SOC. JAPAN **15** (1960) 363~364

Some Properties of X-ray damaged Rochelle Salt

By Kenkichi OKADA

Department of Natural Science, Nagoya Branch, Aichi Gakugei University, Nagoya

(Received November 11, 1959)

Peculiar changes in the ferroelectric hysteresis loops of radiation-damaged ferroelectric crystals have been investigated by a few workers^{1,2)}. The present author observed in X-ray damaged rochelle salts that crystals polarized partially before irradiation have double but asymmetrical hysteresis loops, that domain walls are strongly clamped, and that by application of moderate dc field Curie points shift in directions opposite to those of virgin rochelle salts.

The X-ray tube had a tungsten target and a beryllium window, and was running at 50 kV and 11 mA. A-cut crystals were of 15 mm square and 1.3 mm thick. Gold foil electrodes were short-circuited and the temperature of the crystals was 10°C during X-ray irradiation.

Perfectly polarized single domain crystals prepared by application of strong dc field revealed biased ferroelectric hysteresis loops, but partially polarized crystals revealed double but asymmetrical loops after X-ray irradiation. When symmetrically polarized crystals having no resultant polarization were damaged, symmetrical double loops were obtained. It was suggested that the ratio of the

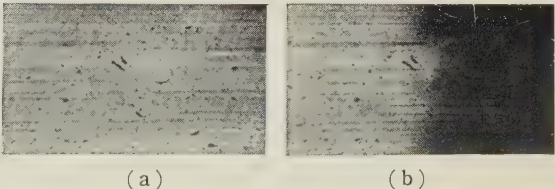


Fig. 1. Clamping effects of domain walls of X-ray damaged rochelle salts. The left halves were damaged by 3 hours X-ray irradiation, while the right halves were kept virgin. In (a) no dc field was applied and in (b) a dc field of 150 V/cm was applied parallel to the a-axis.

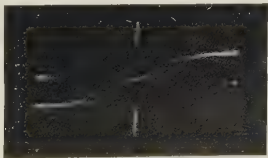


Fig. 2. Typical double hysteresis loop of a rochelle salt damaged by 3 hours X-ray irradiation. The amplitude of 60 cps ac was 1240 V/cm, and the ordinate was 0.37 μ coul/cm².

heights of the two loops forming the double loop is equal to that of the volumes of oppositely polarized domains.

Tightly clamped domain walls of damaged crystals were observed by a polarizing microscope. Application of dc field below 200 V/cm could not move domain walls of crystals damaged by 1 hour-irradiation. Fig. 1 illustrates this clamping effect of domain walls. In the left halves of the photographs (a) and (b) the crystal was damaged by 3 hours-irradiation, while in the right it was kept virgin. In (b) a dc field of 150 V/cm was applied, and it was seen that the virgin part was almost a single domain, but in the damaged part no movement of domain walls occurred. Under a strong dc field of about 1500 V/cm the whole crystal became a single domain.

Relation between the dielectric constant and temperature of a crystal damaged by 3 hours-irradiation, which had a symmetrical double loop as shown in Fig. 2, was measured at 1000 cps. Its peak values were 1070 and 900 at the upper and lower Curie points respectively. When a moderate dc field was applied during the measurements, the peak values at the upper and lower Curie points

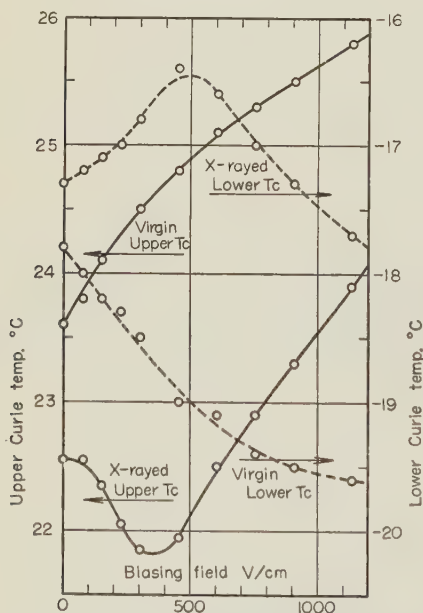


Fig. 3. Effects of biasing field on the Curie points of an X-ray damaged rochelle salt and a virgin rochelle salt.

increased to 1250 and 1200 respectively, and the upper Curie point shifted to low temperature side, while the lower Curie point to high temperature side. Relations between these Curie points and the biasing field are shown in Fig. 3. These phenomena similar to those of antiferroelectrics were

caused probably by clamped domain walls mentioned above. When strong biasing fields were applied, the blurring of the peaks, the shift of their positions and the decrease in their heights occurred in the same manner as in the case of ferroelectric virgin crystals.

References

- 1) I. S. Zheludev and V. A. Iurin: Bull. Acad. Sci. U. S. S. R. **21** (1957) 336. (English translation)
- 2) A. G. Chynoweth: Phys. Rev. **113** (1959) 159.

J. PHYS. SOC. JAPAN **15** (1960) 364~365

Lower Excited States in P^{29}

By Tatsuo TABATA, Hisae FUKUDA
and Kotoyuki OKANO

Department of Physics, Faculty of Science,
Kyoto University, Kyoto

(Received November 28, 1959)

Lower excited states in the isobaric nuclides Si^{29} - P^{29} are of interest as to whether the single nucleon description outside of a closed $d_{5/2}$ shell may be adequate or the collective interpretation of the level sequence may be employed. We have investigated γ -rays from the $Si^{28}(p, \gamma)P^{29}$ reaction at the $E_p=367$ kev resonance, corresponding to the 3.12-MeV level in P^{29} , which had been reported to decay mainly to the first and second excited states in P^{29} ¹⁾.

Extra pure metallic silicon powder was pressed onto a copper backing and was bombarded with a proton beam up to 100 μ A from a Cockcroft-Walton generator. γ -rays were detected with a $5''\phi \times 4''$ NaI crystal and a 100-channel or a 10-channel pulse height analyzer. Energy calibration was carried out using radioisotopes: ThC'' , Y^{88} , Sb^{124} , Na^{22} and Zn^{65} . Four γ -rays of energies $1.96_1 \pm 0.015$ MeV, $1.73_1 \pm 0.010$ MeV, $1.38_4 \pm 0.008$ MeV and $1.15_5 \pm 0.008$ MeV were apparently observed, with relative intensities of 25, 70, 78 and 28 (all $\pm 10\%$), respectively. These energies and relative intensities support the cascade scheme as shown in Fig. 1, which had been suggested by Van Oostrum *et al.* ¹⁾ The direct ground state transition from the resonance state was less than 2% of the total decay. Other cascade decay was also estimated to be weak, if present.

The angular distribution of each γ -ray line was measured by analyzing the spectra taken at 15° intervals with the front face of the crystal 10 cm apart from the target. γ -ray yield was monitored by an integrated proton current and various backgrounds were subtracted by taking the spectra just above and below the resonance. Angular distribu-

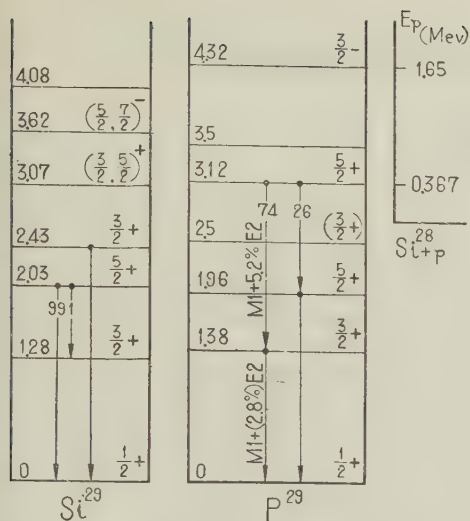


Fig. 1. Level scheme of the mirror pair P^{29} - Si^{29} .

itions of the cascade lines decaying through the first excited state were found to be as follows, after the correction for finite solid angle of the detector and absorption of the target backing:

1.73 Mev:

$$1 - (0.81 \pm 0.18)P_2(\cos \theta) + (0.03 \pm 0.07)P_4(\cos \theta) .$$

1.38 Mev:

$$1 - (0.57 \pm 0.02)P_2(\cos \theta) - (0.02 \pm 0.03)P_4(\cos \theta) .$$

These distributions uniquely fix the resonance state to be $J=5/2+$, formed by a d -wave capture, and the first excited state to be $J=3/2$, which must be

of even parity to be consistent with the results obtained from the stripping reaction³. This $J=3/2+$ assignment is in accord with that for the first excited state in Si^{29} ^{3,4}. The $E2$ to $M1$ mixing ratios determined are cited in Fig. 1. The second excited state at 1.96 MeV is expected to be $J=5/2+$, since the corresponding level in Si^{29} was assigned to be $J=5/2+$ ⁴. It was found, however, that the measured distribution of the 1.16 MeV-1.96 MeV cascade lines, i.e. $1 + (0.37 \pm 0.04)P_2(\cos \theta) + (0.10 \pm 0.07)P_4(\cos \theta)$, and $1 + (0.21 \pm 0.04)P_2(\cos \theta) + (0.12 \pm 0.04)P_4(\cos \theta)$, respectively, cannot be fitted with the $5/2+ (DQ)5/2+(Q)1/2+$ scheme. Unlikely admixture of $M3$ component to $E2$ of several per cents is necessary for the second transition in order to accord with the calculated coefficient of P_2 , although because of the presence of the coefficient of P_4 , $J=5/2+$ assignment to the 1.96 MeV level seems to be valid from the present measurements. The more detailed presentation and discussion of the results will appear later.

References

- 1) K. J. Van Oostrum, J. Alster, N. Zazewindus and A. H. Wapstra: *Physica* **24** (1958) 1051.
- 2) J. M. Calvert, A. A. Jaffe and E. E. Maslin: *Proc. Phys. Soc. London* **A, 70** (1957) 78.
- 3) H. Roderick, O. Lönsjö and W. E. Meyerhof: *Phys. Rev.* **97** (1955) 97.
- 4) D. A. Bromley, H. E. Gove, E. B. Paul, A. E. Litherland and E. Almquist: *Canad. J. Phys.* **35** (1957) 1042.

Errata

Angular Distributions of Protons from the Reaction $^{12}C(\alpha, p)^{15}N$

By Itaru NONAKA, Hisashi YAMAGUCHI, Takashi MIKUMO, Iwao UMEDA, Tatsuo TABATA and Saburo HITAKA
J. Phys. Soc. Japan **14** (1959) 1260

Page	Column	Line	Should be read
1264	left	Fig. 3, caption	$\theta_{lab}=50^\circ$
		Fig. 4, caption	$\theta_{lab}=40^\circ$
	right	Fig. 5, caption	$R=3.67 \times 10^{-13}$ cm
			$R=5.58 \times 10^{-13}$ cm
1266	right	8, 3 and 2 from the bottom	6.41×10^{-13} cm
			5.58×10^{-13} cm
			3.67×10^{-13} cm

PROGRESS OF THEORETICAL PHYSICS

CONTENTS

Progress of Theoretical Physics

Vol. 21, No. 3, March 1959

Theory of Classical Fluids: Hyper-Netted Chain Approximation. II. — <i>Formulation for Multi-Component Systems</i> —.....	Tohru MORITA..361
Spin-Orbit Potential with Pion Scattering Correction.....	S. OKUBO and S. SATO..383
Electrostatic Interactions in an Electron-Ion Gas at High Density.....	Toshiyuki NISHIYAMA..389
Interactions of Hydromagnetic Waves	Yusuke KATO..409
On the Kirkwood Superposition Approximation.....	Ryuzo ABE..421
The Unified Model for Si^{29}	S. P. PANDYA..431
Impurity Effect in Superconductors	Ki-ichi NAKAMURA..435
Global Symmetry and Isotopic Spin Conservation in Non-Feptonic Hyperon Decays	G. TAKEDA and M. KATO..441
Determination of the Pion-Nucleon Coupling Constant by means of the Nucleon- Nucleon Dispersion Relation.....	Sadahiko MATSUYAMA..452
Letters to the Editor:	
A Note on Polarized Cross Section of High Energy n - d Elastic Scattering.....	Y. SAKAMOTO..459
A Remark concerning the Bogoliubov Theory	J. M. BLATT..461
Comment on (p, n) Cross Sections	R. NAKASIMA and H. WATANABE..462
Momentum Dependence of the Healing Distance	T. TAGAMI..465
On the Intermediate Resonance Levels in the Nuclear Reactions	S. IGARASI, K. IZUMO and T. UDAGAWA..468
New Equation of Spin $1/2$ Particles and Isomorphism between Various Transformations	Z. TOKUOKA..471
Origin of Cosmic Rays Revealed in the Rigidity Spectrum of Primary Particles	S. HAYAKAWA and M. KOSHIBA..573
Equation of State of Classical Electron Gas	R. ABE..475
Field Theoretical Interpretation of Multiple Meson Production	T. IMAMURA and K. KOBAYAKAWA..477
Molecular Processes induced by μ -Mesons in Hydrogen Bubble Chamber. II— <i>Mechanisms of Formation of μ-Mesonic Hydro- gen Molecular Ion</i> —.....	Y. MIZUNO, T. IZUYAMA and M. SHIMIZU..479
Errata: Dispersion Relations and Vertex Properties in Perturbation Theory (Vol. 20, p. 690).....	K. SYMANZIK..481
The Clebsch-Gordan Coefficients (Vol. 20, p. 798).....	S. DATTA MAJUMDER..481
Contents of Journ. Phys. Soc. of Japan, Vol. 14, No. 1	482

Price	\$ 1.25 per copy
	\$ 15.00 per year (postage inclusive)
Annual dues for foreign members (individual subscribers)	\$ 12.00 (postage inclusive)
for foreign members of the Physical Society of Japan	\$ 10.00 (postage inclusive)

Application for members, subscriptions and orders for back numbers should
be sent, directly or through book-dealers, to

The Publication Office

in

Yukawa Hall, Kyoto University, Kyoto, Japan

Energy Spectrum and Angular Distributions of Neutrons from the Reaction $\text{Be}^9(p, n)\text{B}^9$ at 8 to 14 MeV of Proton Energies

By Yoshio SAJI

*Institute for Nuclear Study, University of Tokyo,
Tanashi-machi, Tokyo*

(Received October 23, 1959)

The $\text{Be}^9(p, n)\text{B}^9$ reaction has been studied by using a fast neutron spectrometer with a hydrogen gas radiator.

The energy spectrum of neutrons from the reaction at 14.1 MeV of proton energy was obtained and three new excited levels (3.07, 4.14 and 4.94 MeV) in B^9 were observed. They are consistent with the levels of the mirror nucleus, Be^9 , and the level scheme of intermediate coupling model introduced by Kurath.

Moreover, the angular distributions of the $\text{Be}^9(p, n)\text{B}^9$ neutrons at 8.1 to 14.1 MeV of proton energies were obtained. The results do not agree with the theory of Austern, Butler and McManus. The isotropic parts of the neutron angular distributions become larger as the incident proton energies decrease. It is probably due to the fact that, in the lower energy region, the formation of compound nucleus is more preferable.

§ 1. Introduction

The experimental data about (p, n) reaction have been comparatively less than those about the other reactions because of the technical difficulties. The most efforts¹⁾ have been made to obtain the total cross section and nuclear temperature of this reaction for various target nuclei and to compare the results with the statistical theory introduced by Weisskopf. The agreement between the experiments and the theory is good. And those experiments have been carried out mainly by emulsion or activation method.

Only a few works have been carried out to determine the levels by using the (p, n) reaction and to obtain the angular distributions of neutrons from this reaction.

Inglis²⁾ has proposed the intermediate coupling model and Kurath³⁾ has also treated the model in the case of $1p$ -shell and strongly requested to obtain more experimental identifications in the neighbour of Be^9 and B^{11} nuclei to test the model further.

In the Be^9 nucleus, many levels have been observed. Ajzenberg and Buechner⁴⁾ observed the 2.37 MeV level in B^9 with emulsion. Marion, Cook and Bonner,⁵⁾ using two counter technique, confirmed this level and observed a broad level at 1.4 MeV in addition. Recently, Adelson⁶⁾ has reported more eight broad levels at higher energy region. His work

was carried out with a bubble chamber bombarding beryllium with protons of 31.5 MeV. However, it seems that his results may have some ambiguity because of the poor resolution.

On the other hand, Austern, Butler and McManus⁷⁾ have introduced an interesting theory with regard to the angular distribution of protons from the (n, p) reaction. Since the (p, n) reaction is a reverse process to the above mentioned reaction, their theory can be applicable to this reaction. However, these have been few experiments in which measurements have been performed at so many angles that any comparison with the theory is possible. Moreover, the energy dependencies of the angular distributions of the reaction particles have become important from the point of interpretation of the reaction mechanism.

In the present work, the neutron energy spectrum of the $\text{Be}^9(p, n)\text{B}^9$ reaction was studied and some new levels of B^9 were observed. And these levels were compared with the intermediate coupling model. The angular distributions of the $\text{Be}^9(p, n)\text{B}^9$ neutrons at various proton energies (8 to 14 MeV) were also investigated and the results were compared with the theory.

This work has been carried out with the 160 cm variable energy cyclotron at the Institute for Nuclear Study, University of Tokyo.

§ 2. Fast Neutron Spectrometer

As the neutron detector, a proton recoil neutron spectrometer with gas radiator was used. The construction is shown in Fig. 1. As a radiator of recoil protons, hydrogen gas is used, because of the largest density of hydrogen atoms for the same stopping power. Hydrogen gas of 6 kg/cm^2 in pressure is filled in a steel cylinder of 5 cm in length and 2 cm in diameter with a hemispherical cap. This corresponds to energy loss of 2.4% for 10 MeV protons.

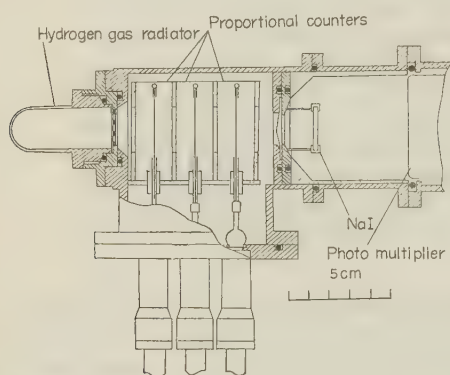


Fig. 1. Structure of the proton recoil fast neutron spectrometer with hydrogen gas radiator.

In order to hold the high gas pressure tight, a 10 micron nickel foil is stretched on the bottom of the hydrogen gas vessel, which has nineteen holes of 3 mm in diameter arranged as a beehive within a circle of 16 mm in diameter. This hole system gives 75% transmission for passing particles.

Three proportional counters, used in quadruple coincidence with a scintillator of sodium iodide crystal, are set between the radiator and the scintillator. Each counter is separated from each other by 1 micron nickel foils. Argon- CO_2 (5%) gas mixture is filled in the counter to 14 cm Hg. It is found that the use of multiple proportional counters is very efficacious to eliminate the background pulses.

The cavity for the scintillator is constructed with especially light metal, aluminium, to reduce the γ -ray background and is painted by white enamel made of titanium oxide. A sodium iodide crystal is suspended in the cavity, not directly on the photomultiplier tube, in order to avoid the effect of non-uniform sensitivity of the photocathode surface. The defining aperture of the scintillator cavi-

ty is 13 mm in diameter and covered with a 10 micron nickel foil. The distance between the radiator and the aperture of the scintillator cavity is 84 mm.

The energy loss of the recoil protons by various materials throughout the path to the scintillator is calculated to obtain the correct neutron energy spectrum. It is estimated as 0.8 MeV for 10 MeV protons and 1.3 MeV for 5 MeV protons.

The total energy resolution of the neutron spectrometer is about 5%, but in the best condition, it reaches to 3%.

It is somewhat complicated to estimate the counter efficiency and the solid angle subtended at the target, because of the considerably large extension of the radiator and of the existence of the beehive structure through which the recoil protons must pass. Fig. 2 shows the notations of the calculation for the solid angle. Assuming that the hydrogen gas is all condensed at the bottom of the container,

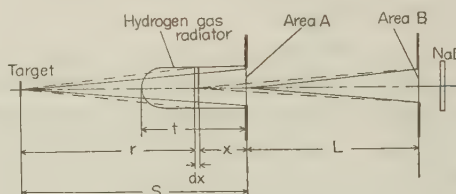


Fig. 2. Solid angle subtended by the spectrometer at the target. The notations are used in the calculation of the solid angle.

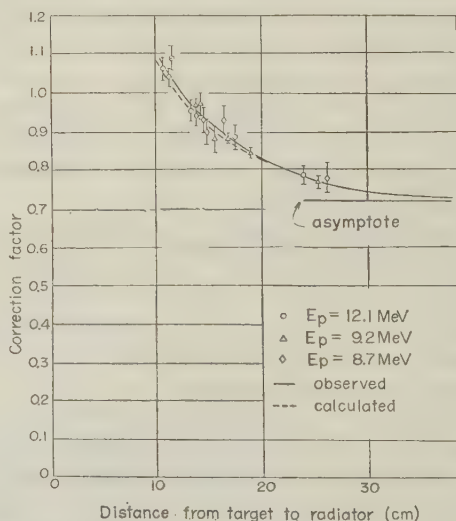


Fig. 3. Correction factor for the solid angle subtended by the spectrometer at the target. The picture also shows the comparison of the calculated results with the experiment.

a simple calculation gives the solid angle as follows:

$$\Omega_0 = AB \frac{1}{S^2} \frac{1}{L^2} \quad (1)$$

But, in order to carry out a detailed calculation, the following expression is given,

$$\Omega = \frac{AB}{\int_0^t dt} \int_0^t \frac{1}{(S-x)^2} \frac{1}{(x+L)^2} dx \quad (2)$$

In order to compare the equations with the experiment, the distance from the target to the detector was varied. The values of the cross section from the experiments are calculated by Eq. (1) and are represented in Fig. 3. If the approximation of Eq. (1) was good, each experimental point should have same value along the longitudinal axis, that is a value of unity as a correction factor. The result shows bad agreement. Then, the correction has been made by Eq. (2) and the result is represented by the dashed curve. The agreement with the experiment is very good. However, in the region very close to the target, some disagreement appears, probably due to the neutrons scattered by the wall of the target chamber. In practice we used Eq. (2), corrected by the experiments.

The absorption of neutrons in the material which construct the walls of the target chamber and of the hydrogen gas container is calculated by assuming that the absorption is given by the total cross section of the neutrons in those materials.

The efficiency of this spectrometer is estimated to be 8.9×10^{-6} for 10 MeV neutron.

§ 3. Experimental Arrangement

The proton beam is suitably focussed on the target by means of the quadrupole magnets and is defined by a graphite slit at a distance apart from the target. The target chamber is made of a thin walled (1mm thick) steel pipe and is protected against undue neutrons and γ -rays by heavy shields of paraffin and concrete blocks. A long pipe, 2 meter in length and isolated electrically, follows the chamber and has a graphite stopper at the end. This long pipe also plays the role of the beam current monitor.

The spectrometer can be rotated around the target and the distance from the target can also be varied.

As the neutron monitor, a BF_3 proportional

counter is placed at the 90° direction.

The beam current was 0.3 to 1.5μ Amp., and the beam spot on the target was 2mm in width and 15mm in height. The background at the neutron spectrometer was negligibly small, being much less than 1% for the ground state peak.

Thin beryllium metal foils (8mg/cm² and 16mg/cm² thick) are used as the targets.

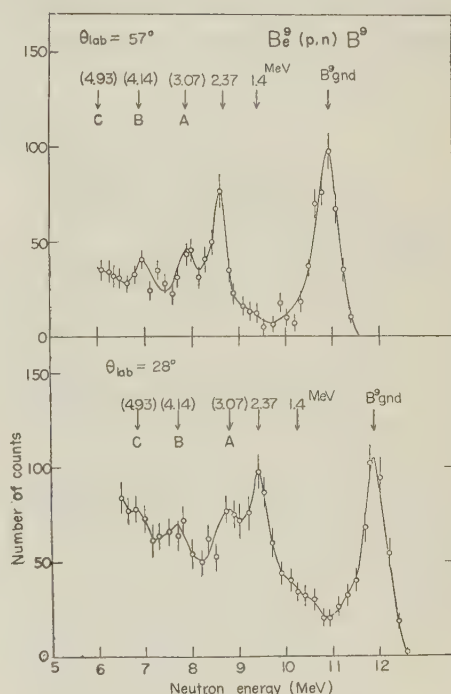


Fig. 4. Neutron energy spectra from the $\text{Be}^9(p, n)\text{B}^9$ reaction at 14.1 MeV of incident proton energy at 28 and 57 degrees in laboratory angle.

§ 4. Results and Discussion

Firstly, the energy spectrum of $\text{Be}^9(p, n)\text{B}^9$ neutrons was studied. Fig. 4 shows some examples of the neutron energy spectra. As the results, the known levels (1.4 and 2.37 MeV levels) of B^9 were confirmed and in addition, more three new levels have observed. The evidences of these levels have been confirmed at each angle of observation.

These new levels are as follows:

- A 3.07 MeV
- B 4.14 MeV
- C 4.93 MeV

The error of the energy scale is estimated to be less than 0.1 MeV. However, the existence

of 4.93 MeV level is somewhat ambiguous.

In this experiment, the (p, pn) reaction is energetically possible. The background in the lower energy region is considered to be partially due to the continuous distribution of the neutrons from these (p, pn) reaction.

The angular distributions of the neutrons from the $\text{Be}^9(p, n)\text{B}^9$ reaction corresponding to the ground state of B^9 were obtained at various energies of the incident protons. Fig. 5 shows the results.

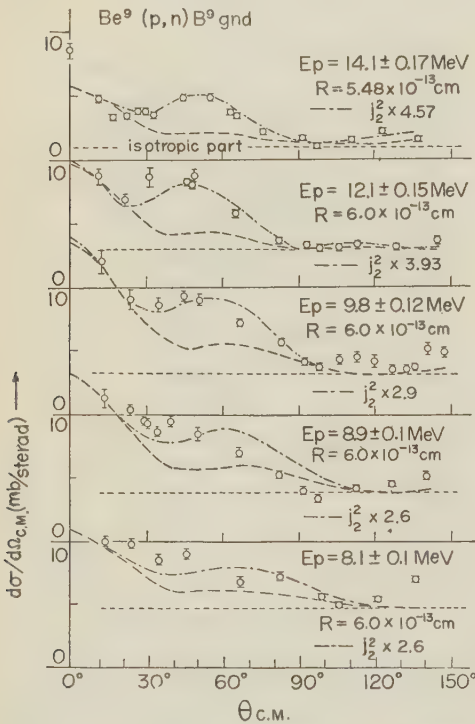


Fig. 5. Angular distributions of $\text{Be}^9(p,n)\text{B}^9$ neutrons corresponding to the ground state of B^9 at 8.1 to 14.1 MeV of incident proton energies. The dashed curves represent the calculation following the theory of Austern, Butler and McManus. The dash- and dotted curves represent the semi-experimentally fitted curves.

In order to compare the results with the theory introduced by Austern, Butler and McManus,⁷⁾ a calculation has been carried out following the formula given by them:

$$\sigma(\theta) \propto \sum_l C_{l_n l_p}^2(l, 0; 0, 0) \{j_l(kR)\}^2$$

where $C_{l_n l_p}$ is Clebsch-Golden coefficient. In our case, the expression becomes follows

$$\sigma(\theta) \propto \frac{1}{3} [j_0^2(kR) + 2j_2^2(kR)]$$

Actually, following to the analysis on the (d, p) reaction by Evans and French,⁸⁾ the isotropic part of the angular distribution was subtracted from the experimental results and compared with the calculation. The results calculated are represented with dashed curves in the figure. The agreement between the experimental results and the calculation can not be said to be good. However, if the second term, j_2 , might be multiplied by an

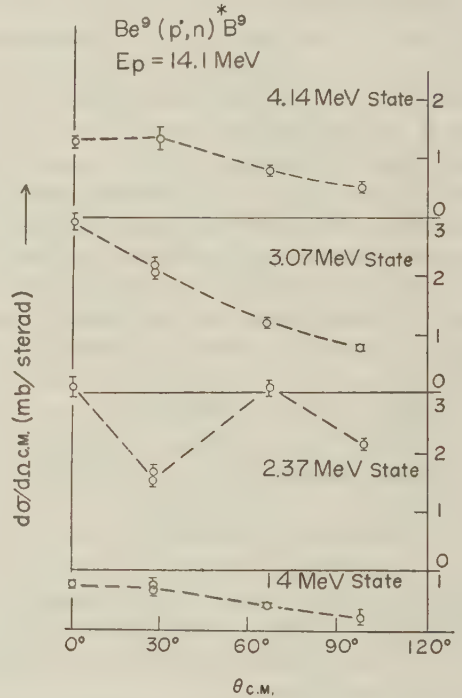


Fig. 6. Angular distributions of the $\text{Be}^9(p,n)\text{B}^9$ neutrons corresponding to 1.4, 2.37, 3.07 and 4.14 MeV excited states of B^9 at 14.1 MeV of incident proton energy.

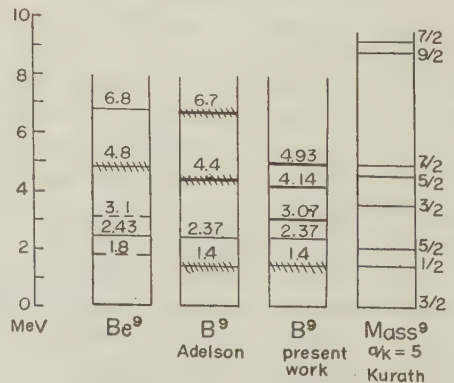


Fig. 7. Comparison of the observed levels in B^9 with the levels of Be^9 , the intermediate coupling model scheme calculated by Kurath and the levels obtained by Adelson.

appropriate factor to fit the experimental points, the dash and dotted curves would be obtained.

Moreover, the angular distributions of the neutrons corresponding to some excited states (1.4, 2.37, 3.07 and 4.14 MeV states) of B^9 at 14.1 MeV of incident proton energy were also obtained. They are shown in Fig. 6. However, since the experimental points are too less, the comparison with the theory is not made.

For comparison, the observed levels of B^9 , those of the mirror nucleus Be^9 , the theoretical level scheme calculated by Kurath⁸⁾, and the levels obtained by Adelson⁶⁾ are shown in Fig. 7. It seems that the correspondency of the present results to the others is comparatively good.

On the other hand, the observed angular distributions of the $\text{Be}^9(p, n)\text{B}^9$ neutrons do not agree with the theory of Austern, Butler and McManus. In an experiment⁹⁾ following this, it was found that the disagreement was also seen for the $\text{B}^{11}(p, n)\text{C}^{11}$ reaction. Then, it is concluded that the assumptions made in the above mentioned theory can not be applicable to such a lighter nuclei.

It was also observed that the isotropic parts of the neutron angular distributions were larger as the incident proton energies decreased. It is probably due to that, in the lower

energy region, the formation of compound nucleus is more preferable.

Acknowledgements

The author wishes to express his sincere thanks to Prof. I. Nonaka for his constant encouragement and to Drs. A. Isoya, Y. Ishizaki, Y. Nakano, K. Yuasa, T. Nakamura, B. Saheki and K. Hisatake for their kind helps throughout this work. His thanks are also due to the cyclotron operators of the Institute for their efforts to maintain the suitable cyclotron operation.

References

- 1) for examples, J. P. Blaser, F. Boehm, P. Marmier and P. Scherrer: *Physica Acta* **24** (1951) 441. P. C. Gugelot: *Phys. Rev.* **81** (1951) 51. B. L. Cohen: *Phys. Rev.* **98** (1955) 49. H. G. Blosser and T. H. Handley: *Phys. Rev.* **100** (1955) 1340.
- 2) D. R. Inglis: *Rev. Mod. Phys.* **25** (1953) 390.
- 3) D. Kurath: *Phys. Rev.* **101** (1956) 216.
- 4) F. Ajzenberg and W. W. Buechner: *Phys. Rev.* **91** (1953) 674.
- 5) J. B. Marion, C. F. Cook and T. W. Bonner: *Phys. Rev.* **94** (1954) 807.
- 6) H. E. Adelson: UCRL 8568 (1958).
- 7) N. Austern, S. T. Butler and H. McManus: *Phys. Rev.* **92** (1953) 350.
- 8) N. T. S. Evans and A. P. French: *Phys. Rev.* **109** (1958) 1272.
- 9) to be published: *J. Phys. Soc. Japan*.

Decay of $\text{Cl}^{34\text{m}}$

By Tsutomu TÔHEI

*Department of Physics, Faculty of Science,
Tohoku University, Sendai*

(Received November 6, 1959)

The gamma rays following the decay of chlorine 34 were studied with the scintillation spectrometer using a $4''\phi \times 4''$ NaI(Tl) crystal and a Sunvic 100 channel pulse height analyser. Samples were produced with a betatron by the $\text{Cl}^{35}(\gamma, n)\text{Cl}^{34}$ reaction. In the search gamma rays of 1.17 Mev, 2.14 Mev, 3.32 Mev and weak three gamma rays of 0.64 Mev, 0.77 Mev, and 4.10 Mev were found. The relative intensities are obtained as follows: $I(1.17 \text{ Mev}) : I(2.14 \text{ Mev}) : I(3.32 \text{ Mev}) : I(4.10 \text{ Mev}) = 32:100:32:1.0$.

§ 1. Introduction

The gamma rays following positron decay of $\text{Cl}^{34\text{m}}$ were found by H. K. Ticho¹⁾ and it was quite well established by P. Stähelin et al.²⁾ that they decayed from the $3^+(T=0)$ isomeric state of Cl^{34} . Although the studies for the lower excited states of S^{34} were well performed by many authors³⁾ and the first and the second excited states were assigned to be 2^+ states by means of gamma-gamma angular correlation, search for the higher excited state was only reported by H. Morinaga and E. Bleuler⁴⁾. They did not determine the energy of the 4.0 Mev gamma ray exactly because of a small NaI crystal which they used.

Recently, the higher excited states of S^{34} were well observed by $\text{Cl}^{37}(p, \alpha)\text{S}^{34}$, $\text{P}^{31}(\alpha, p, \gamma)\text{S}^{34}$ reaction etc..⁵⁾ Therefore, it is of interest to determine the origin of the weak high energy gamma ray and to see whether the weak gamma rays emitted from the higher excited states are in cascade or not.

§ 2. Experimental Procedure and Results

Samples of Cl^{34} were produced with the betatron of Tohoku University by the $\text{Cl}^{35}(\gamma, n)\text{Cl}^{34}$ reaction. The threshold energy of the $\text{Cl}^{35}(\gamma, n)\text{Cl}^{34}$ reaction was 12.3 Mev and the maximum energy of the giant resonance was 17 Mev and therefore, we bombarded the extra pure NaCl or CCl_4 samples with the 24 Mev bremsstrahlung. In such case we did not find any observable impurity radiation as expected. In the case of CCl_4 we used the method of Szilard-Chalmer. The method has frequently been used to obtain radioactive samples of high specific activity, and in our

case the free Cl^{34} produced by the (γ, n) reaction were extracted by shaking it with an aqueous reducing solution containing a trace of free Cl as a carrier, and it was deposited as AgCl by filtration through fine paper. Almost all the measurement, however, were done by irradiated NaCl samples without chemical separation. The half-life measured by a G-M counter was 32.4 minutes, and other possible activities were not detected.

The gamma ray scintillation spectrometer consisted of a 4 inch $\phi \times 4$ inch cylindrical NaI(Tl) crystal mounted on a DuMond 6364 photomultiplier. For the pulse height analysis a Sunvic 100 channel pulse height analyzer was used. In this measurement the gamma rays were collimated by a cylindrical aperture of 5 cm $\phi \times 10$ cm long in the lead shield, and in order to eliminate the 4.5 Mev positron back ground it was necessary to place a 2.8 g/cm² polystyrene absorber between the sample and the crystal. The positron absorption experiment of Cl^{34} beta rays proved that the 4.5 Mev positrons have the range of 2.4 g/cm² in Al. In order to measure accurately the high energy gamma rays, linearity test of the scintillation spectrometer was necessary for the high energy parts. For this purpose, the gamma rays of Cs^{137} , Zn^{65} , Na^{22} , Co^{60} , Na^{24} , and Po-Be 4.45 Mev gamma ray were used as the energy calibration. The result showed the linearity to be very good. It was also used the two gamma rays of 1.37 Mev, 2.75 Mev, and their sum peak 4.12 Mev, in the well-known Na^{24} decay.

To determine the intensity ratio, the detection efficiency of the $4''\phi \times 4''$ long NaI cry-

stal in the present geometry were obtained from the total efficiency*⁶⁾ and the photo-fractions. The photo-fractions were determined by the photopeak ratio to the total spectrum of the various standard gamma rays under conditions similar to this experiment. The 0.51 Mev annihilation gamma rays in the case of Zn^{65} , Na^{22} were substrated from the total spectrum.

For the check of intensity calibration curve, the two Co^{60} gamma rays were measured and agreed within 4% error to the expected value assuming that the angular distribution of the cascade gamma rays of Co^{60} are isotropic. When the source were placed in front of the collimator slit, it was observed that the sum peak produced with cascade gamma rays amounted to 4% in this geometry. The results are shown in Fig. 1. Present data shows the lower photo-fractions than the one of Kreger's data⁷⁾ for high energy part, but it could not compare with his data, because his collimating system was more narrow and he did not observe the gamma ray above 2.7 Mev. His results agreed to the Miller's theoretical calculation⁸⁾ by the Monte Carlo method. In these cases, however, we could not but to use these present experimental

data where the gamma ray entered in the broadening cone to the crystal. In Fig. 2, there are the high energy portion of the gamma ray spectrum in Cl^{34} which was measured with a single crystal.

This set-up are more useful to measure the high energy gamma rays, especially for reducing the sum and escape peaks. In this spectrum, 1.17 Mev, 2.14 Mev, 3.32 Mev and 4.10 Mev peaks were observed, and errors were ± 0.02 Mev. The peaks with no arrow were the over-up peaks of their one quantum escape and Compton peak. The intensity ratio were measured as follows; 1.17 Mev: 3.32 Mev: 4.10 Mev = 32:32:1.0, assuming 2.14 Mev as 100 units.

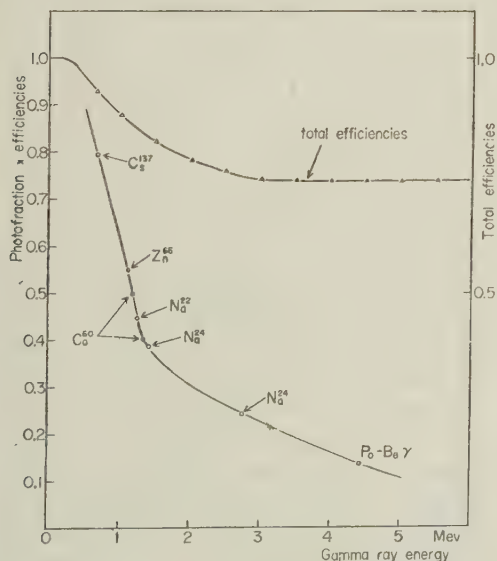


Fig. 1. Total efficiency curve and the photo-fraction curve multiplying the total efficiency, of $4''\phi \times 4''$ NaI crystal. The photo-fractions were determined experimentally in the present geometry.

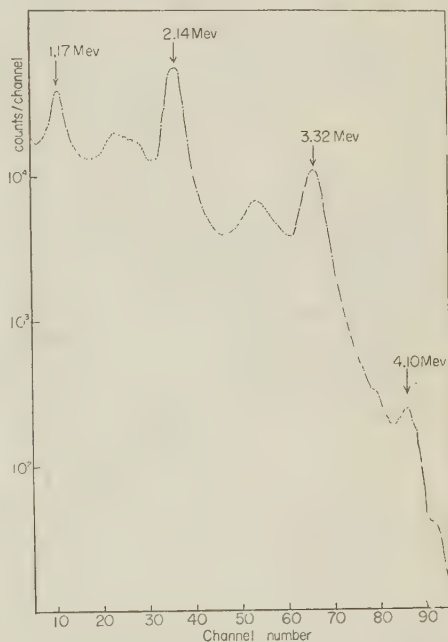


Fig. 2. The high energy portion of scintillation spectrum taken by the 100 channel pulse height analyzer.

The coincidence measurement was performed by making use of the Sunvic 100 channel pulse height analyzer. In the case of slow coincidences, the gamma ray spectrum of main detector using $1\frac{1}{2}''\phi \times 1\frac{1}{2}''$ NaI crystal as a head was displayed on the 100 channel pulse height analyzer, gated by the pulse from the single channel pulse height analyzer using $4''\phi \times 4''$ NaI crystal as a gate detector. The gamma ray coincidence measurements were also made by using a "fast-slow" coincidence circuit⁹⁾ of which the resolving time

* It modified from the N. B. S. data.

$2\tau=30$ m μ sec. The results are shown in Fig. 3, 4, and 5. In Fig. 3, the coincidence spectrum gated with 1.17 Mev photopeak by the "fast-slow" coincidence circuit is shown in Fig. 3. 2.14 Mev, 1.17 Mev, 0.77 Mev, 0.64 Mev and 0.51 Mev gamma rays were found. The gamma ray of 1.17 Mev must be coincidence with the tail of the gamma ray of 2.14 Mev and in each run two unknown peaks of 1.0 Mev and 1.3 Mev were observed at the place where it must be a valley. The gamma ray of 0.51 Mev is the annihilation peak of the positrons which precede to the gamma transition. The gamma ray spectrum in

company the Compton peak at the same place. The 0.51 Mev peak is the annihilation

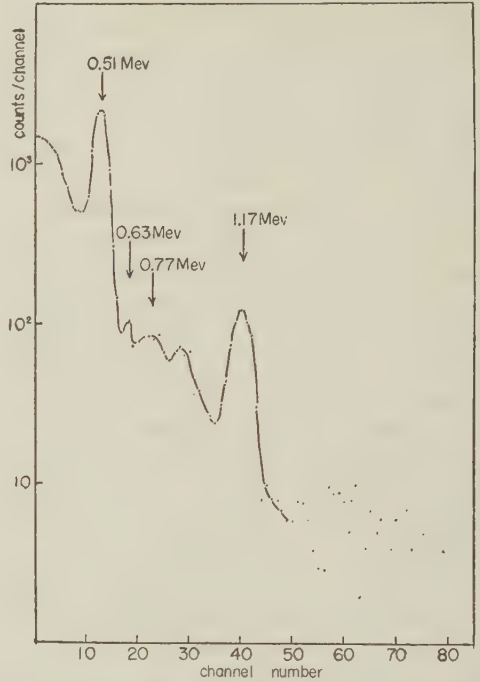


Fig. 4. Coincidence spectrum with 2.14 Mev photopeak.

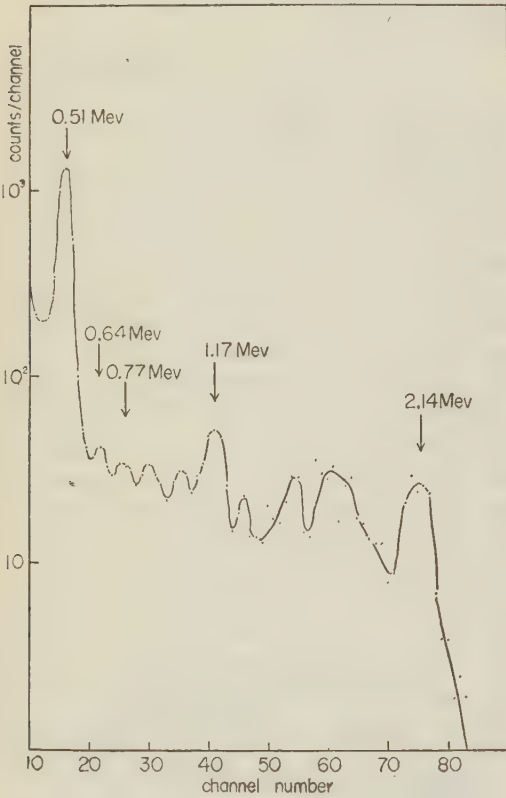


Fig. 3. Coincidence spectrum with 1.17 Mev photopeak.

slow coincidence with 2.14 Mev photopeak is shown in Fig. 4. The chance coincidences were subtracted in this spectrum. In Fig. 4, 1.17 Mev, 0.77 Mev, 0.63 Mev, and 0.51 Mev peaks were clearly resolved. The fact that the peak with no mark was the Compton peak of the 1.17 Mev gamma ray was confirmed. The 1.12 Mev gamma ray of Zn^{65} and the 1.17 Mev gamma ray in coincidence with 1.33 Mev of Co^{60} were also shown to ac-

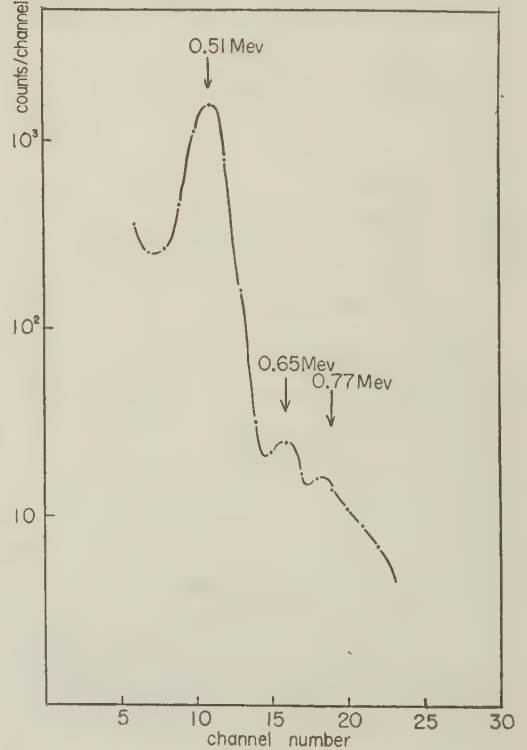


Fig. 5. Coincidence spectrum with 3.32 Mev photopeak.

peak. Fig. 5 shows the gamma ray spectrum in slow coincidence with the 3.32 Mev photo-peak. The chance coincidences were also subtracted in this spectrum. In it, 0.77 Mev, 0.65 Mev and 0.51 Mev peaks were found. According to the above coincidence experiments we confirmed the new gamma rays of 0.77 Mev, 0.64 Mev, which were very weak, in coincidence with the gamma rays of 1.17 Mev, 2.14 Mev and 3.32 Mev. In addition, as well known, the gamma ray of 1.17 Mev was in coincidence with that of 2.14 Mev.

§ 3. Conclusion

A proposed decay scheme of $\text{Cl}^{34\text{m}}$ is presented in Fig. 6.

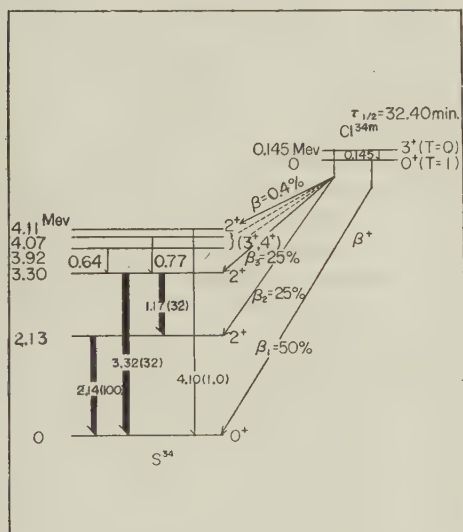


Fig. 6. Proposed decay scheme of $\text{Cl}^{34\text{m}}$.

The 4.0 Mev gamma ray, reported by reference 4, is replaced for its position by the 4.10 Mev gamma ray for the transition from the 4.11 Mev state to the ground state. The very weak gamma ray of 0.64 Mev may be the cascade for the transition from the 3.92 Mev state to the 3.30 Mev state. The similar gamma ray of 0.77 Mev may be the cascade for the transition from the 4.07 Mev state to the 3.30 Mev state. These level are in fairly good agreement with the levels reported by P. M. Endt et al.⁵⁾. The intensity ratio assuming the 2.14 Mev gamma ray as 100 unit is shown in Fig. 6. The intensity ratio slightly differ from those of Green's data³⁾.

However, the positron branching ratio to each state calculated from our gamma ray

intensity, agrees with the values measured by the magnetic spectrometer³⁾. Using the value of the 4.5 Mev positron branching for the $0^+ \rightarrow 0^+$ transition from the ground state of Cl^{34} to the ground state of S^{34} , by the beta spectrometer, the positron branching ratio to the 1st and the 2nd excited states amount to 25% and 25% of the total decay respectively, hence they are quite in agreement with their experiments³⁾.

Also the positron branching for the decay from the isomeric state of Cl^{34} to the 4.11 Mev state of S^{34} is estimated to be about 0.4% of the total decay and the log f - t -value of the positron decay to the 4.11 Mev state is 5.15 ± 0.20 . The state found at 4.10 Mev is assigned to be a 2^+ state, but the 3.92 Mev and 4.07 Mev states may be expected to be 3^+ or 4^+ states. It is remarkable that there are many 2^+ states in such light even-even nuclei, as Mg^{26} , Si^{28} , S^{32} , S^{34} etc.

The author hopes to express his appreciation to Professor M. Kimura for his encouragement and interest in the search. He expresses his sincere thanks to Professor H. Morinaga for suggestions and interest in the search. He is also indebted to Mr. N. Mutsuro for his helpful discussions and to the betatron-group for their kind cooperations.

References

- 1) H. K. Ticho: Phys. Rev. **84** (1951) 847. L. Ruly and J. R. Richardson: Phys. Rev. **83** (1951) 698.
- 2) W. Arber and P. Stähelin: Helv. Phys. Acta **26** (1953) 584. P. Stähelin: Helv. Phys. Acta **26** (1951) 691. D. C. Peaslee: Nuovo Cimento **10** (1953) 1349. S. A. Moszkowski and D. C. Peaslee: Phys. Rev. **93** (1954) 455. D. C. Kinster and B. M. Rustad: Phys. Rev. **114** (1959) 1329. D. Strominger, J. M. Hollander and G. T. Seabourg: Rev. Mod. Phys. **30** (1958) 616.
- 3) H. E. Handler and J. R. Richardson: Phys. Rev. **102** (1956) 833. D. Green and J. R. Richardson: Phys. Rev. **10** (1956) 776. D. Green: thesis, University of California, Los Angeles (unpublished).
- 4) H. Morinaga and E. Bleuler: Phys. Rev. **103** (1956) 1423.
- 5) P. M. Endt, C. M. Paris, A. Sperduto, and W. W. Buechner: Phys. Rev. **103** (1956) 961. G. S. Stanford and G. F. Pieper: Phys. Rev. **103** (1956) 637.

- 6) M. Mimura, N. Mutsuro, Y. Ohnuki, K. Sioda, M. Sugawara, T. Tohei and H. Yuta: J. Phys. Soc. Japan **14** (1959) 387.
- 7) W. E. Kreger: Phys. Rev. **96** (1954) 1554.
- 8) W. F. Miller, J. Reynold and W. J. Snow: Rev. Sci. Instr. **28** (1957) 717.
- 9) H. Morinaga, N. Mutsuro and M. Sugawara: Phys. Rev. **114** (1959) 1146.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 3, MARCH, 1960

Ferromagnetism of an Electron Gas

By Masao SHIMIZU

Department of Physics, Tokyo Metropolitan University

(Received August 1, 1959)

Magnetism, especially ferromagnetism, of an electron gas is studied on the basis of the Bohm-Pines collective description of electron interactions. Exchange interactions are derived from the screened Coulomb interaction, the interaction obtained from the second-order perturbation of the screened Coulomb interaction, and the weak interaction coming from the interaction between plasma and individual electrons. We assume effective mass for the electron mass. The total energy of the electron gas in the ferromagnetic state is compared with that in the non-ferromagnetic state, and the conditions of ferromagnetism for the electron gas are discussed. The one-electron approximation being adopted, the effective number of magnetic carriers in the electron gas is expressed as a function of temperature and magnetic field. Using the Weiss approximation, we express the spontaneous magnetization at an arbitrary temperature in terms of this effective number and the molecular field obtained from the proper average of the exchange interactions. At low temperatures, the spin-wave approximation is adopted. The Curie temperature, the paramagnetic susceptibility above the Curie point, and the temperature variation of spontaneous magnetization at low temperatures are determined as functions of the effective mass and the electron mean distance. Using the effective masses determined so as to explain the experimental values of the electronic heats, we make a comparison with experimental values for Ni, Co and Fe. It shows satisfactory agreement in the case of positive hole gas. The strong paramagnetism of γ Fe, Pd and Pt are also satisfactorily explained, and the inverse of their susceptibilities is well expressed as the sum of a constant term and the term proportional to T^2 at comparatively lower temperatures.

§ 1. Introduction

Ferromagnetism of conduction electrons was first studied by Bloch¹⁾, according to whom singly-occupied electrons in the neighbourhood of the Fermi surface were considered to be carriers of ferromagnetism, and the exchange interaction of the Coulomb interaction between them was regarded to be an origin of ferromagnetism of conduction electrons. The mean magnetic moment was calculated by the same statistical method as the Heisenberg

theory²⁾ and conditions of ferromagnetism at the absolute zero of temperature were discussed. The collective electron ferromagnetism has been so far worked out in detail by Stoner³⁾, Wohlfarth⁴⁾, Lidiard⁵⁾, and others. It was assumed that the ferromagnetism of the transition metals was due to holes in the 3d band and a molecular field proportional to the magnetization worked on them. This phenomenological theory has been very successful in explaining the experimental values

by adjusting the degeneracy temperature and the coefficient of the molecular field. Lidiard⁵⁾ has tried to obtain the second-order transition of collective electron ferromagnetism from the exchange interaction, and tried to find an origin of the molecular field. Taking the actual band structure into account Slater⁶⁾ has studied the ferromagnetism of transition metals.

In the Stoner theory, the temperature variation of spontaneous magnetization at low temperatures is generally proportional to T^2 , and if in the ground state one of the two directions of spin has either only a completely filled or a completely empty band of electrons, the approach to saturation is exponential. It is also shown that the excess specific heat due to ferromagnetism is proportional to the temperature. According to the few experimental facts available, the variation of magnetization is found to be proportional to $T^{3/2}$ at low temperatures and to T^2 at slightly high temperatures. It is well-known that this $T^{3/2}$ law is deduced from the spin-wave theory⁷⁾ in which the electron spins get on rigid lattice points, and the specific heat of spin wave is proportional to $T^{3/2}$. Although the spin-wave theory has been warranted in the case of insulators where the electron spins are localized⁸⁾, it has been thought that there is an excitation like a spin-wave in the metals also, and Herring and Kittel⁹⁾ have shown that the mode of spin-wave motion should exist in metals if there is the energy increase due to the fluctuation of magnetization in space as in a domain wall. The coefficient of the energy increase, that is, the Bloch wall coefficient for the electron gas, has been calculated by Herring¹⁰⁾. As it is apparent that there is no spin-wave in an ideal free electron gas in which the Coulomb interaction does not work, the Coulomb interaction, or the exchange interaction, seems to be indispensable to the spin-wave motion, but it is not clear whether it is indispensable in the Herring calculation or not. And Herring and Kittel⁹⁾ have pointed out that there are both types of excitations, the electron orbital motion over the Fermi surface and the spin-wave motion, in a ferromagnetic transition metal. They have also pointed out that at low temperatures, the lower power of temperature in the tempera-

ture variations of spontaneous magnetization and of specific heat will predominate, that is, the former will be proportional to $T^{3/2}$ and the latter to T . These are in accord with experimental facts. According to their suggestion we regard the exchange interaction to be necessary to the spin-wave motion, and taking into account the orbital motion and the spin-wave motion simultaneously, we discuss the ferromagnetism of an electron gas. At any rate the individual spin magnetic moments are not constants of motion when there are exchange interactions between them, but in Stoner's theory they have been treated as if they were so, and the spin-wave mode has never appeared.

Recently Bohm and Pines¹¹⁾⁻¹³⁾ have developed a collective description of electron interactions. The long-range part of the Coulomb interaction is described by plasma oscillations and there remains among individual electron motions only the short-range part of the interaction, which is the screened Coulomb interaction. Pines has calculated the exchange energy of the screened Coulomb interaction and long-range and short-range correlation energies.¹³⁾ He has compared the energies of the electron gas in a ferromagnetic state and in the normal state showing as a result that the electron gas would not be ferromagnetic at any electron density. It will be probable that the electron gas having a real electron mass does not show ferromagnetism at any electron density and the spin wave excitation obtained by Herring in the electron gas becomes unstable because of the correlation.

In this paper we study the ferromagnetism and the paramagnetism of an electron gas having an effective mass in which the collective nature of the gas is taken into consideration. The coefficients of the molecular fields which are assumed in the Stoner theory are determined from the Bohm-Pines collective description of electron interactions. In the statistical-mechanical or the thermodynamical treatment of an electron gas, the respective effects of the exchange interaction and correlation on the one-electron state density must be taken care of, whenever we attribute the origin of the molecular field to these interactions. In §2 using the vector model, we consider the problem of the spin multiplicity in an electron gas. In §3 we treat the ex-

change interaction of the screened Coulomb interaction. The mean values of the exchange integrals over the singly-occupied electrons are calculated in the case of the degenerate electron gas. In §4 the short-range correlation energy derived from the second-order perturbation of the screened Coulomb interaction is treated, and the exchange integral of this short-range correlation interaction is discussed. The exchange integral of the weak velocity-dependent interaction which comes from the perturbation of the interaction between plasma oscillations and individual electrons is treated also. From the calculations of the exchange energy and the correlation energy, done in §3 and §4, conditions for the ferromagnetism of an electron gas having effective mass are discussed in §5. In §6 we calculate the effective number of magnetic carriers, that is, the number of singly-occupied electrons, as a function of temperature and magnetic field. In §7 by the same method as Heisenberg's²⁾ and Bloch's¹⁾, the mean magnetization of a ferromagnetic electron gas is given. Formulas for the Curie temperature and the paramagnetic susceptibility above the Curie point are obtained. The condition of obtaining positive Curie temperature is discussed. The spin-wave motion of the singly-occupied electrons and the temperature variation of spontaneous magnetization due to the motion are considered in §8. In §9 the experimental results of the ferromagnetic transition metals, Ni, Co, Fe, are compared with the results obtained in §7 and §8, by taking two models of gas, an electron gas and a positive hole gas. The effective mass of the electron (or positive hole) gas is determined so as to be consistent with the observed value of the electronic specific heat at low temperatures. In §10 the strong paramagnetism of γ Fe, Pd, Pt and its temperature dependence are analyzed, and their effective masses and their effective numbers of carriers (electrons or positive holes) are fixed.

§2. Vector Model of an Electron Gas

We consider an aggregate of N electrons embedded in a background of uniform positive charge, whose density is equal to that of the electrons. A configuration of these N electrons in the momentum space is assumed

to be such that only n electrons singly occupy the levels and the remaining $N-n$ electrons doubly occupy the levels according to the two directions of spin. There are 2^n spin multiplicities in this configuration as each electron has its spin angular momentum. If we use the vector model and are satisfied with the Weiss approximation, the problem of spin multiplicity becomes simple.

The spin Hamiltonian for the above configuration of electrons may be written

$$\mathcal{H} = E_0 - \frac{1}{2} \sum_{\lambda > \mu} (1 + 4\mathbf{s}_\lambda \cdot \mathbf{s}_\mu) J_{\lambda\mu}, \quad (2.1)$$

where E_0 represents the sum of kinetic energy, the Coulomb energy and the interaction energy between the electrons and the uniform positive charge. $\mathbf{s}_\lambda$ and $\mathbf{s}_\mu$ are spin operators of the electrons which have wave vectors $\mathbf{k}_\lambda$ and $\mathbf{k}_\mu$ respectively. $J_{\lambda\mu}$ is an exchange integral of the electron orbits λ and μ . This summation is to be extended over only all the orbits occupied singly by electrons.

If the temperature is low enough for the electron gas to be degenerate and the magnetic field is not so strong, the singly-occupied electrons will be confined in the neighbourhood of the Fermi surface (cf. §6). If in (2.1) $J_{\lambda\mu}$ is replaced by the mean value,

$$\mathcal{H} = E_0 - \langle J_{\lambda\mu} \rangle_{AV} \{n(n-4)/4 + S^2\}, \quad (2.2)$$

where $\mathbf{S} = \sum_{\lambda=1}^n \mathbf{s}_\lambda$ is the total spin angular momentum operator of the singly occupied electrons, and

$$\langle J_{\lambda\mu} \rangle_{AV} = 2 \sum_{\lambda > \mu} J_{\lambda\mu} / n(n-1). \quad (2.3)$$

As $S^2 = S(S+1)$, where S is the total spin quantum number of n electrons, the result (2.2) is the same as that obtained already by Bloch¹⁾. The eigen value of the Hamiltonian (2.2) can be easily obtained. Then the mean magnetic moment of the electron gas is calculated as a function of n . We can make use of the Heisenberg method as well as Bloch which corresponds to the Weiss approximation. When an external magnetic field $\mathbf{H}_0$ is present, the Zeeman energy, $-g\mu_B \mathbf{H}_0 \cdot \mathbf{S}$, is added to (2.1). Then the mean magnetic moment M is given by

$$M = (g\mu_B n/2) \tanh \{g\mu_B (H_0 + \alpha M)/\kappa T\}, \quad (2.4)$$

where

$$\alpha = 2 \langle J_{\lambda\mu} \rangle_{AV} / g^2 \mu_B^2. \quad (2.5)$$

(2.4) can be directly derived from the Hamiltonian (2.2) by making use of the Weiss approximation.

§ 3. Exchange Interaction of the Screened Coulomb Interaction

According to the Bohm-Pines theory,¹¹⁾⁻¹³⁾ the interaction between electrons becomes short-range and the one between i and j electrons is given by

$$(4\pi e^2/V) \sum_{k > k_c} k^{-2} \exp \{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)\}, \quad (3.1)$$

where V is the total volume of the electron gas and k_c is the maximum collective oscillation wave vector. Let the magnitude of the wave vector at the Fermi surface be k_0 , and $\beta = k_0/k_0$ in the non-magnetic state of an electron gas was determined by Ferrell¹⁴⁾ and Sawada et al.¹⁵⁾ such as

$$\beta = k_0/k_0 = 0.47 r_s^{1/2}, \quad (3.2)$$

where r_s is the inter-electronic spacing measured in units of the Bohr radius, a_0 . r_s is given by $4\pi r_s^3 a_0^3/3 = V/N$.

In the magnetic state the maximum wave vector of plasma oscillation will depend on the magnetization. When all electrons have the same direction of spin, from the dispersion relation of plasma oscillation and the condition that the plasma solutions are unstable, we approximately obtain

$$\omega \approx k_0' k_0' / m, \quad (3.3)$$

where k_0' and k_0' are the maximum wave

vectors of plasma oscillation and the degenerate Fermi distribution in this magnetic case respectively, that is, $k_0' = 2^{1/3} k_0$, and ω is the plasma frequency and is approximately given by $\omega_p = (4\pi e^2 N/mV)^{1/2}$. Then, from (3.2) and (3.3) we have

$$\beta' = k_0'/k_0' = 2^{-2/3} \beta = 0.30 r_s^{1/2}. \quad (3.4)$$

On the other hand, also in the magnetic case where only a part of electrons has the same direction of spin, the maximum wave vector of plasma oscillation will certainly depend on the magnetization, but the relation between them has not been found yet. In the case where the net magnetization per electron is small, it will be unexpected that k_0 depends on magnetization strongly, so that we assume that the maximum wave vector, k_0 , is independent of magnetization in this case. It will be supposed that the maximum wave vector of plasma oscillation and accordingly the screening distance change with temperature in the ferromagnetic case, as the magnetization should decrease with increasing temperature.

As we shall see latter, there are various exchange interactions, but first we consider an ordinary exchange integral of the interaction (3.1). The exchange integral between the orbits, which are described by the unperturbed one-electron wave functions, namely plane waves with wave vectors $\mathbf{k}_\lambda$ and $\mathbf{k}_\mu$, is given by¹²⁾

$$\left. \begin{aligned} J_{\lambda\mu}^{s,c} &= (4\pi e^2/V)(\mathbf{k}_\lambda - \mathbf{k}_\mu)^{-2}, & \text{if } |\mathbf{k}_\lambda - \mathbf{k}_\mu| > k_0; \\ &= 0, & \text{if } |\mathbf{k}_\lambda - \mathbf{k}_\mu| < k_0. \end{aligned} \right\} \quad (3.5)$$

When the electron gas is assume to be completely degenerate, the one-electron energy of wave vector $\mathbf{k}$ nearly on the Fermi surface becomes¹²⁾

$$\left. \begin{aligned} \mathcal{E}(\mathbf{k}) &= \mathcal{E}_K(\mathbf{k}) + \mathcal{E}_{ex}(\mathbf{k}), \\ \mathcal{E}_K(\mathbf{k}) &= \hbar^2 k^2 / (2m^*), \\ \mathcal{E}_{ex}(\mathbf{k}) &= -\frac{e^2 k_0}{2\pi} \left\{ 1 + \frac{k_0^2 - k^2}{k k_0} \log \left(\frac{k + k_0}{\beta k_0} \right) + \frac{3k^2 - k_0^2}{2k k_0} - 2\beta + \frac{\beta^2 k_0}{2k} \right\}, \end{aligned} \right\} \quad (3.6)$$

where the periodic lattice field is partly taken into account by using an effective mass m^* of the electron gas.

In order to obtain $\langle J_{\lambda\mu} \rangle_{Av}$, (2.3) from $J_{\lambda\mu}^{s,c}$, (3.5), we average $J_{\lambda\mu}^{s,c}$ over n states occupied singly by electrons. We sum (3.5) over the electrons with the wave vectors such as $k_- < k_\lambda < k_+$ and $k_- < k_\mu < k_+$, where we assume $k_+ > k_- > k_0$, and $k_0 > k_+ - k_-$. We find, on changing the sums to integrals,

$$\frac{1}{2} \sum_{\lambda, \mu} J_{\lambda\mu}^{s,c} = \frac{Ve^2}{16\pi^3} \left\{ (k_+ - k_-)^4 / 4 + (k_+^2 - k_-^2)^2 \log \left(\frac{k_+ + k_-}{k_0} \right) \right\}. \quad (3.7)$$

At a normal temperature these singly-occupied electrons are considered to be in the neighbourhood of the Fermi surface, as the electron gas of an ordinary density is almost completely degenerate. If all the states between k_+ and k_- are singly occupied, we have

$$(N+n) = (V/3\pi^2)k_+^3, \quad (N-n) = (V/3\pi^2)k_-^3, \quad N = (V/3\pi^2)k_0^3. \quad (3.8)$$

In the case of $n \ll N$, $\langle J^{s.c.} \rangle_{Av}$ is approximately given by

$$\langle J^{s.c.} \rangle_{Av} = (2e^2 k_0 / 3\pi N) \log(2/\beta). \quad (3.9)$$

This is the average of the exchange integrals of the screened Coulomb interaction over the Fermi surface. From the above formula, the coefficient of the molecular field, (2.5) is written as

$$\alpha^{s.c.} = 2g^{-2} \mu_B^{-2} \langle J^{s.c.} \rangle_{Av} = (4e^2 k_0 / 3\pi g^2 \mu_B^2) \log(2/\beta). \quad (3.10)$$

When the interactions between electrons are not short-range but long-range, the average of the exchange integrals of the long-range interactions becomes $\langle J_{\lambda\mu} \rangle_{Av} = (2e^2 k_0 / 3\pi N) (\log(3N/n) + 3/2)$, by calculation similar to (3.9). As compared with (3.9) this is so large when $n \ll N$ that it becomes meaningless. This absurd result is due to the anomaly of the state density on the Fermi surface when the long-range Coulomb interaction is used.

The total exchange energy of the screened Coulomb interaction also was given by Pines² such as

$$E_{exch}^{s.c.} = -(3e^2 k_0 N / 4\pi) \left(1 - \frac{4}{3}\beta + \frac{1}{2}\beta^2 - \frac{1}{48}\beta^4 \right), \quad (3.11)$$

where electrons doubly occupy up to the levels with k_0 , namely $n=0$. When $n=N$ and all electrons have the same direction of spin, we have instead of (3.8), $N = (V/6\pi^2)k_0'^3$, and

$$E_{exch}^{s.c.}(N) = -(3e^2 k_0' N / 4\pi) \left(1 - \frac{4}{3}\beta' + \frac{1}{2}\beta'^2 - \frac{1}{48}\beta'^4 \right). \quad (3.12)$$

In this case the average of the exchange integrals is written from (2.3) and (3.12) as

$$\langle J^{s.c.} \rangle_{Av} = (3e^2 k_0' / 2\pi N) \left(1 - \frac{4}{3}\beta' + \frac{1}{2}\beta'^2 - \frac{1}{48}\beta'^4 \right), \quad (3.13)$$

and we have for the coefficient of the molecular field,

$$\alpha^{s.c.} = (3e^2 k_0' / \pi g^2 \mu_B^2 N) \left(1 - \frac{4}{3}\beta' + \frac{1}{2}\beta'^2 - \frac{1}{48}\beta'^4 \right). \quad (3.14)$$

When $n \neq 0$, $n \ll N$, and these n electrons have parallel spins, from (3.8) and (3.11), the total exchange energy is expanded in powers of n/N as follows:

$$E_{exch}^{s.c.}(n) = E_{exch}^{s.c.} + (e^2 N / 2a_0) (n/N)^2 \gamma_{s.c.} + \dots, \quad (3.15)$$

$$\gamma_{s.c.} = -0.204\gamma_s^{-1} + 0.01125. \quad (3.16)$$

§ 4. Exchange Interaction due to the Short-Range Correlation

Pines¹³ has shown that the effect of short-range correlation on various physical properties of materials is important. Recently the corrections due to this effect have been examined by Fletcher and Larson¹⁰. This correlation is derived from the second-order perturbation theoretic calculation of the screened Coulomb interaction, (3.1). When the electron gas is completely degenerate, we have the interaction energy due to the short-range correlation between electrons with wave vectors k_1 and k_2 by the vector model as

$$\varepsilon(\mathbf{k}_1\mathbf{k}_2) = -\frac{m}{\hbar^2} \left(\frac{4\pi e^2}{V} \right)^2 \sum_{\mathbf{p}} \left\{ \frac{1}{p^4 \mathbf{p} \cdot (\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)} - \frac{\frac{1}{2}(1 + 4\mathbf{s}_1 \cdot \mathbf{s}_2)}{p^2(\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)^2 \mathbf{p} \cdot (\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)} \right\}, \quad (4.1)$$

where the sum over wave vector $\mathbf{p}$ is restricted by the Pauli principle to the regions: $|\mathbf{p} + \mathbf{k}_1| > k_0$; $|\mathbf{p} + \mathbf{k}_2| > k_0$; $p > k_0$, and the second term in the sum is subject to an additional restriction, $|\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2| > k_0$. As Pines¹³⁾ pointed out, the free electron mass is taken in (4.1) instead of the effective mass, because not only the intra-band but the inter-band matrix elements of the screened Coulomb interaction must be included in (4.1). This approximation is important to obtain ferromagnetism of the electron gas, and without this approximation we cannot expect ferromagnetism of the electron gas as shown in §5.

The interaction energy for electrons of antiparallel spin is given by the first term in the sum (4.1). The interaction energy for electrons of parallel spin may likewise be given by (4.1) in which $\frac{1}{2}(1 + 4\mathbf{s}_1 \cdot \mathbf{s}_2)$ is equal to one. The total short-range correlation energy, when electrons doubly occupy up to the levels with k_0 , is

$$E_{corr}^{s,r} = -\frac{m}{\hbar^2} \left(\frac{4\pi e^2}{V} \right)^2 \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \sum_{\mathbf{p}} \left\{ \frac{2}{p^4 \mathbf{p} \cdot (\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)} - \frac{1}{p^2(\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)^2 \mathbf{p} \cdot (\mathbf{p} + \mathbf{k}_1 + \mathbf{k}_2)} \right\}, \quad (4.2)$$

where the regions of the sum are given by the restrictions identical with those for (4.1) and $k_1 < k_0$, $k_2 < k_0$. This energy was first evaluated by Pines¹³⁾, and Gell-Mann and Brueckner¹⁷⁾ have made it more accurate.

The one-electron energy $\varepsilon(\mathbf{k})$ is also influenced by the short-range correlation and this part has been given by Fletcher and Larson¹⁶⁾ as the sum of the parallel spin contribution, $\varepsilon_{s,r}^p(\mathbf{k})$, and the antiparallel spin contribution, $\varepsilon_{s,r}^a(\mathbf{k})$,

$$\varepsilon_{s,r}(\mathbf{k}) = \varepsilon_{s,r}^a(\mathbf{k}) + \varepsilon_{s,r}^p(\mathbf{k}). \quad (4.3)$$

Because the formula for $\varepsilon_{s,r}(\mathbf{k})$ is fairly involved, we do not express $\varepsilon_{s,r}(\mathbf{k})$ explicitly in this paper and the reader is referred to the paper of Fletcher and Larson¹⁶⁾ (cf. Eqs. (8d) and (8e)). We can neglect $\varepsilon_{s,r}^p(\mathbf{k})$, since $\varepsilon_{s,r}^p(\mathbf{k})$ is small compared to $\varepsilon_{s,r}^a(\mathbf{k})$, in actual electron densities of most metals. For the high-density limit ($r_s \rightarrow 0$), we can take $\varepsilon_{s,r}^p(\mathbf{k}) \approx \varepsilon_{s,r}^a(\mathbf{k})$ ¹⁹⁾. Then, the one-electron energy (3.6) should be rewritten as

$$\varepsilon(\mathbf{k}) = \varepsilon_K(\mathbf{k}) + \varepsilon_{ex}(\mathbf{k}) + \varepsilon_{s,r}(\mathbf{k}). \quad (4.4)$$

From (4.1), we find an exchange interaction between electrons with wave vectors $\mathbf{k}$ and $\mathbf{k}'$ in addition to the exchange interaction of the screened Coulomb interaction (3.1), and the exchange integral is given by

$$J_{\mathbf{k}\mathbf{k}'}^{s,r} = -\frac{m}{\hbar^2} \left(\frac{4\pi e^2}{V} \right)^2 \sum_{|\mathbf{p}| > k_0} \frac{1}{p^2(\mathbf{p} + \mathbf{k} + \mathbf{k}')^2 \mathbf{p} \cdot (\mathbf{p} + \mathbf{k} + \mathbf{k}')}, \quad (4.5)$$

where the regions of the sum are identical with those of (4.1).

Moreover, Bohm and Pines^{11), 13)} have shown that the weak velocity dependent electron-electron interaction is deduced from the second-order perturbation-calculation of the electron-plasma interaction. An exchange integral of this interaction is approximately given by

$$\left. \begin{aligned} J_{\mathbf{k}\mathbf{k}'}^{r,p} &= -(\pi e^2 \hbar^2 / V m^2) (k^2 - k'^2)^2 (\mathbf{k} - \mathbf{k}')^{-2} / \{ \omega^2 - \hbar^2 (k^2 - k'^2)^2 / 4m^2 \}, & \text{if } |\mathbf{k} - \mathbf{k}'| < k_0; \\ &= 0, & \text{if } |\mathbf{k} - \mathbf{k}'| > k_0, \end{aligned} \right\} \quad (4.6)$$

where ω is the plasma frequency,

$$\omega^2 = \omega_p^2 + k^2 \langle v^2 \rangle_{Av} + \hbar^2 k^4 / (4m^2), \quad (4.7)$$

and $\langle v^2 \rangle_{Av}$ is the average of the squares of electron velocities over the Fermi distribution. It should be noted that the exchange integrals $J_{\mathbf{k}\mathbf{k}'}^{s,r}$, (4.5), and $J_{\mathbf{k}\mathbf{k}'}^{r,p}$, (4.6), have negative values. This arises from the fact that the first-order exchange integral $J_{\mathbf{k}\mathbf{k}'}^{s,c}$, (3.5), has a

positive value and this positive value is reduced by the perturbation theory.

We average next the exchange integrals (4.5) and (4.6) over the singly-occupied levels. The mean value of $J_{kk'}^{r,p}$ is obtained as in the case of $J_{kk'}^{s,c}$, but if $n \ll N$ the order of magnitude of the mean value is smaller by n/N than (3.9). Then we neglect $J_{kk'}^{r,p}$ when $n \ll N$. In order to get the mean value of $J_{kk'}^{s,r}$, we make use of the results obtained by Gell-Mann and Brueckner¹⁷⁾ and Nozières and Pines¹⁸⁾,

$$(3/16\pi^5) \int d^3k \int d^3p \int d^3q \{k^2(k+p+q)^2 k \cdot (k+p+q)\}^{-1} = 0.046 - 0.015\beta^2, \quad (4.8)$$

where energy is measured in Rydberg units, wave vectors are measured in units of k_0 and the regions of integration are $p < 1$; $q < 1$; $k > \beta$; $|p+k| > 1$; $|q+k| > 1$; $|k+p+q| > \beta$. Then the mean value of $J_{kk'}^{s,r}$ over n levels occupied singly by electrons is approximately given by

$$\langle J_{kk'}^{s,r} \rangle_{Av} = 2n^{-2} \sum_{k > k'} J_{kk'}^{s,r} = -(me^4/2\hbar^2 N)(0.184 - 0.060\beta^2). \quad (4.9)$$

The above approximation seems to be rough, but it is inevitable at present as the necessary integrations have not been carried out. From (4.9) the coefficient of the molecular field due to the exchange interaction (4.5) is

$$\alpha^{s,r} = 2g^{-2} \mu_B^{-2} \langle J_{kk'}^{s,r} \rangle_{Av} = -2(me^4/2\hbar^2 g^2 \mu_B^2 N)(0.184 - 0.060\beta^2). \quad (4.10)$$

The total coefficient α when $n \ll N$ is the sum of (3.10) and (4.10), and using the relation (3.2) and $g=2$ we obtain

$$\alpha = (e^2/2a_0 \mu_B^3 N) \{ (0.5898 - 0.2036 \log r_s)/r_s - 0.092 + 0.00663r_s \}. \quad (4.11)$$

When $n=N$ and all electrons have the same direction of spin, the total short-range correlation energy is

$$E_{corr}^{s,r}(N) = -\frac{1}{2} \frac{m}{\hbar^2} \left(\frac{4\pi e^2}{V} \right)^2 \sum_p \sum_k \sum_{k'} \left\{ \frac{1}{p^4 p \cdot (p+k+k')} - \frac{1}{p^2 (p+k+k')^2 p \cdot (p+k+k')} \right\}, \quad (4.12)$$

where the regions of the sum are identical with those of (4.2) except that k_0 and k_c are replaced by k_0' and k_c' respectively. The total energy of the interaction (4.6) also is given by

$$E^{r,p}(N) = -\frac{1}{2} \sum_{k < k_0', k' < k_0'} J_{kk'}^{r,p} = (9N\hbar^2 k_0'^2/32m) \left(\frac{16}{45} \beta'^3 - \frac{1}{2} \beta'^4 + \frac{4}{15} \beta'^5 - \frac{1}{18} \beta'^6 \right). \quad (4.13)$$

The coefficients of the molecular field in this case, $n \approx N$, are given by

$$\alpha_N^{s,r} = 2g^{-2} \mu_B^{-2} N^{-2} \sum_k \sum_{k'} J_{kk'}^{s,r} = -(me^4/2\hbar^2 g^2 \mu_B^2 N)(0.184 - 0.060\beta'^2), \quad (4.14)$$

from (2.3), (2.5) and (4.5), where the regions of the sum are identical with those of (4.2), and

$$\alpha_N^{r,p} = -4(g\mu_B N)^{-2} E^{r,p}(N), \quad (4.15)$$

from (2.3), (2.5) and (4.13). When $n \approx N$, the total coefficient of the molecular field, α_N , the sum of (3.14), (4.14) and (4.15), and from (3.4) and $g=2$, α_N is written as,

$$\alpha_N = (e^2/2a_0 N \mu_B^2) (1.15r_s^{-1} - 0.486r_s^{-1/2} + 0.029 - 0.00200r_s^{1/2} + 0.00125r_s). \quad (4.16)$$

* The term being proportional to β'^5 did not appear in Pines' results^{13,18)}. This term gives the r_s^{-1} term in the correlation energy. Then this should be cancelled by another energy term and we omit this term from (4.13) and the similar term in (4.21), but we remain the similar term in (4.15). Furthermore the coefficient of the term proportional to β'^4 should be corrected by the factor 0.98/0.517 as seen from the higher-order perturbation-calculation¹⁸⁾.

When $n \neq 0$, $n \ll N$, and these n electrons have parallel spins, the total short-range correlation energy of (4.1) is expanded in powers of n/N as follows¹⁹⁾:

$$E_{corr}^{s.r.}(n) = E_{corr}^{s.r.} + (e^2 N / 2a_0)(n/N)^2 r_{s.r.} + \dots, \quad (4.17)$$

$$r_{s.r.} = 0.0580 - 0.0169 \log r_s + 0.000493 r_s. \quad (4.18)$$

The expression (4.18) is in accord with the result obtained for an electron gas at high density by Brueckner and Sawada²⁰⁾. The total exchange energy of (4.6), when $n \ll N$, is also expanded in powers of n/N as¹⁹⁾,

$$E^{r.p.}(n) = E^{r.p.} + (e^2 N / 2a_0)(n/N)^2 r_{r.p.} + \dots, \quad (4.19)$$

$$r_{r.p.} = -0.00562 + 0.0212 r_s^{-1/2} + 0.0000689 r_s, \quad (4.20)$$

$$E^{r.p.} = - \sum_{k < k_0} \sum_{k' < k_0} J_{kk'}^{r.p.} = (9N\hbar^2 k_0^2 / 64m) \left(\frac{16}{45} \beta^3 - \frac{1}{2} \beta^4 + \frac{4}{15} \beta^5 - \frac{1}{18} \beta^6 \right). \quad (4.21)$$

§ 5. Possibilities of Ferromagnetism for an Electron Gas

In this section we discuss the possibilities of the ferromagnetism of an electron gas at $T = 0^\circ\text{K}$. In order to discuss the total energy of an electron gas, we must take kinetic energy into account. Let us consider the kinetic energy of the electron gas which is completely degenerate. When $n = N$, the kinetic energy is

$$E_K(N) = (\hbar^2 / 2m^*) \sum_{k < k_0'} k^2 - (k_0'^3 / 6k_0^3) (\hbar^2 / 2m) \sum_{k < k_0'} k^2. \quad (5.1)^*$$

From (4.7) the zero point energy of the plasma oscillation, when $n = N$, is given by,

$$E_P(N) = \sum_{k < k_c'} \left(\frac{\hbar\omega}{2} - \frac{2\pi e^2 N}{V} \frac{1}{k^2} \right) = \frac{e^2 N}{2a_0} \left\{ -\frac{1.22\beta}{2^{1/3}r_s} + \frac{0.866\beta^3}{2r_s^{3/2}} + \frac{0.705\beta^5}{2r_s^{5/2}} + \frac{0.210\beta^7}{2^{7/3}r_s^{7/2}} \right\}. \quad (5.2)$$

In the case where $n = N$, and all of the electron spins are parallel, from (3.12), (4.12), (4.13), (5.1), and (5.2) the total energy of the electron gas is

$$E(N) = E_K(N) + E_P(N) + E_{exch}^{s.c.}(N) + E_{corr}^{s.r.}(N) + E^{r.p.}(N). \quad (5.3)$$

On the other hand, in the case where $n = 0$, namely electrons doubly occupy up to the level with k_0 , the total energy of the electron gas is given by the sum of the kinetic energy E_K , where

$$E_K = (\hbar^2 / m^*) \sum_{k < k_0} k^2 - (\beta^3 / 6) (\hbar^2 / m) \sum_{k < k_0} k^2, \quad (5.4)$$

and the zero point energy of the plasma oscillation E_P , where

$$E_P = \sum_{k < k_c} \left(\frac{\hbar\omega}{2} - \frac{2\pi e^2 N}{V k^2} \right) = \frac{e^2 N}{2a_0} \left\{ -\frac{1.22\beta}{r_s} + \frac{0.866\beta^3}{r_s^{3/2}} + \frac{0.705\beta^5}{r_s^{5/2}} + \frac{0.210\beta^7}{r_s^{7/2}} \right\}, \quad (5.5)$$

and (3.11), (4.2), and (4.21), that is,

$$E_0 = E_K + E_P + E_{exch}^{s.c.} + E_{corr}^{s.r.} + E^{r.p.}. \quad (5.6)$$

Here we compare the energies (5.3) and (5.6), and let the difference be $\Delta E_N = E(N) - E_0$. The condition, $\Delta E_N < 0$, shows that the total energy of the state in which all the electrons have the same direction of spin is lower than the one of the non-magnetic state. From (3.2) and (3.4) this condition, $\Delta E_N < 0$, is rewritten as,

* The free electron mass m , instead of m^* , is taken in the second term of the right-hand side of (5.1) as well as in (4.1) and (4.6).

$$m/m^* < (r_s/5.466)(1 - 0.2272r_s - 0.01287r_s^2 + 0.1305r_s \log r_s). \quad (5.7)$$

The region which satisfies the condition (5.7) is shown as the upper part of curve (1) in Fig. 1. If we confine the total energy of the electron gas to the kinetic energy and the exchange energy of the screened Coulomb interaction only, the condition corresponding to $\Delta E_N < 0$ becomes $\Delta E_N' = \{E_K(N) + E_{exch}^{s.c.}(N)\} - \{E_K + E_{exch}^{s.c.}\} < 0$, and this is rewritten as $m/m^* < (1 - 0.08766r_s + 0.001956r_s^2)r_s/5.466$, where we

use the approximation that k_0 is independent of magnetization. The region which satisfies this is shown as the upper part of curve (4) in Fig. 1. From this curve it is seen that $\Delta E_N'$ is always positive when $m^*/m=1$. This fact has already been shown by Pines¹²⁾. The condition that corresponds to the Bloch approximation¹⁾ becomes $m/m^* < r_s/5.466$, and this is shown by curve (5) in Fig. 1. It shows that electron gases for which $r_s > 5.466$ and $m^*/m=1$ should be ferromagnetic. As seen from curves (1), (4) and (5) in Fig. 1, the conditions differ much from one another, and this means that the long-range correlation and the short-range correlation have pronounced effects on the possibilities of ferromagnetism of an electron gas. From the above results we obtain the conclusion that if the kinetic energy alone is reduced by the heavy effective mass the ferromagnetism of the electron gas in which all spins are parallel can be stable at $T=0^\circ\text{K}$.

On the other hand, when $n \ll N$ the kinetic energy of the electron gas is

$$\begin{aligned} E_K(n) &= \left(\frac{\hbar^2}{2m^*} - \frac{\beta^3 \hbar^2}{12m} \right) \left(\sum_{k < k_+} k^2 + \sum_{k < k_-} k^2 \right) \\ &= E_K + \frac{e^2 N}{2a_0} \left(\frac{n}{N} \right)^2 r_K, \end{aligned} \quad (5.8)$$

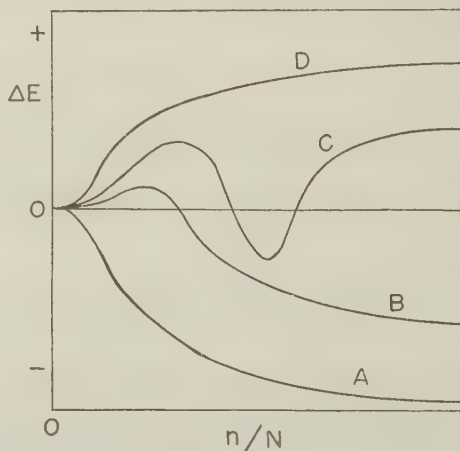


Fig. 2. Schematic diagram of the variations of energy with the degrees of the magnetization, n/N , in the regions A, B, C and D shown in Fig. 1.

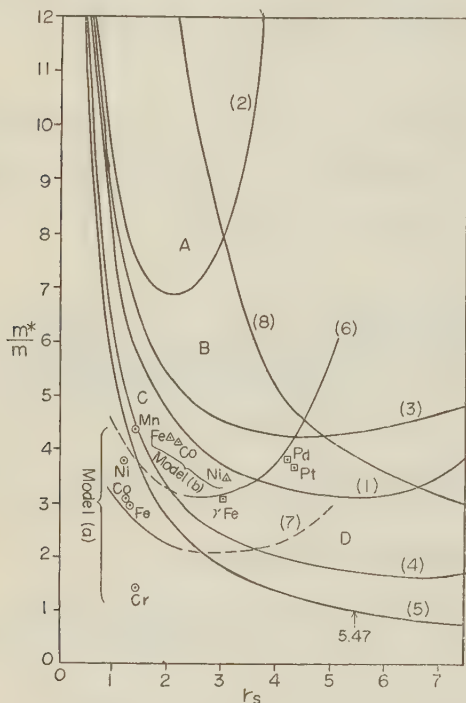


Fig. 1. The energies of the electron gas in various magnetic states are compared at 0°K . Curves (1), (4) and (5) show the relations between r_s and m^*/m when the energy at the largest magnetization, $n=N$, is equal to that at the non-magnetic state, $n=0$. In curve (4), short-range correlation is ignored. In curve (5) the short-range and long-range correlations are ignored. Curves (2) and (3) show the relation between r_s and m^*/m so that just above curves (2) and (3) the energy of the electron gas with the very small magnetization, $n \ll N$, is lower than the energy in the non-magnetic state. Curve (3) corresponds to the high-density limit. Curves (6) and (7) show the relations on which $T_0=0$ for the larger r_s and for the smaller r_s respectively (§ 7). The state density at the Fermi surface becomes zero on curve (8) (§ 11). The circles show the values of m^*/m determined from the electronic specific heats with the model of the electron gas. The triangles show the values of m^*/m determined in the same way with the model of the positive hole gas. The squares show the values of m^*/m and r_s determined from the variation with temperature of susceptibilities for γFe , Pd, and Pt.

$$\gamma_K = 1.228r_s^{-2}(m/m^*) - 0.02124r_s^{-1/2}. \quad (5.9)$$

The zero point energy of the plasma oscillation, when $n \ll N$, is

$$E_P(n) = E_P + (e^2 N / 2a_0)(n/N)^2 \gamma_P, \quad (5.10)$$

$$\gamma_P = 0.008981, \quad (5.11)$$

because $\langle v^2 \rangle_{Av}$ is dependent of magnetization. From (3.15), (3.16), (4.17)–(4.20), (5.8)–(5.11) the total energy in this case is written as, $E(n) = E_0 + (e^2 N / 2a_0)(n/N)^2(\gamma_K + \gamma_P + \gamma_{s,e} + \gamma_{s,r} + \gamma_{r,p})$. The condition, $\Delta E_n = E(n) - E_0 < 0$, or $\gamma = \gamma_K + \gamma_P + \gamma_{s,e} + \gamma_{s,r} + \gamma_{r,p} < 0$, means that the energy of the electron gas becomes lower as long as the electron gas has a net spin moment even if it is very small. The formula, $\gamma < 0$, is rewritten, from (3.16), (4.18), (4.20), (5.9), and (5.11), as

$$m/m^* < (0.204 - 0.0676r_s - 0.000561r_s^2 + 0.0169r_s \log r_s) r_s / 1.23. \quad (5.12)$$

This condition is represented by curve (2) in Fig. 1. The relations between the energy ΔE_n and n/N in the regions denoted by *A*, *B*, *C* and *D* in Fig. 1, are shown in Fig. 2, respectively. It will be expected that in the region *C* the energy ΔE_n will be minimum at the value of n/N such as $0 < n/N < 1$. This will be further discussed in § 7. According to the calculation of the paramagnetic susceptibility of a high-density electron gas by Brueckner and Sawada²⁰), the corresponding condition for the high-density electron gas to (5.12) is $m/m^* < \{0.814r_s + (0.0676 \log r_s - 0.225)r_s^2\} / 4.91$. This is shown by curve (3) in Fig. 1 and is similar to (5.12) in the region where r_s is small, but the difference between them at the larger r_s is considerable. The values m^*/m so as to explain the electronic specific heats of Ni, Co, Fe, Mn, Cr, Pd and Pt are also shown in Fig. 1, and the details will be given in § 9 and § 10. Curves (6) and (7) are explained in § 7 and curve (8) in § 11.

§ 6. Effective Number of Singly-Occupied Electrons

In § 2 it has been assumed that there are a certain number of electrons which occupy levels singly, that is, an effective number of magnetic carriers, and those electrons have spin angular momenta and can play a role in the magnetism of electron gas. It has already been shown that at the absolute zero of temperature and in an external magnetic field, the number of electrons which occupy levels singly is given by the difference between the number of positive and negative spins. Let us define the number of singly-occupied electrons also at an arbitrary temperature. Bloch¹⁾ has already shown a method to determine the number, but we propose another method.

The probability P_γ that the γ th level is singly occupied by an electron equals one minus the probability that the level is doubly occupied by electrons and the probability that the level is entirely empty. That is, P_γ equals to the sum of the probability that the γ th level is singly occupied by an electron of positive spin and the probability that the level is singly occupied by an electron of negative spin. Let the probability that the γ th level of positive spin is occupied by an electron and the probability that the level of negative spin is occupied by an electron be f_γ^+ and f_γ^- respectively. P_γ is written as follows:

$$P_\gamma = 1 - f_\gamma^+ f_\gamma^- - (1 - f_\gamma^+)(1 - f_\gamma^-) = f_\gamma^+(1 - f_\gamma^-) + f_\gamma^-(1 - f_\gamma^+). \quad (6.1)$$

The total number of singly-occupied levels n is

$$n = \sum_\gamma P_\gamma = \int_0^\infty P_\gamma \rho(\epsilon_\gamma) d\epsilon_\gamma = N - 2 \int_0^\infty f_\gamma^+ f_\gamma^- \rho(\epsilon_\gamma) d\epsilon_\gamma, \quad (6.2)$$

where $\rho(\epsilon_\gamma)$ is the energy level density of the electron gas at energy ϵ_γ . When the one-electron energy is known as a function of wave vector $\mathbf{k}$, $\rho(\epsilon)$ is given by,

$$\rho(\epsilon) = (V/2\pi^2)(k^2/(d\epsilon/dk)). \quad (6.3)$$

$f_{\gamma}^{\pm}$ are the well-known Fermi-Dirac distribution functions,

$$f^{\pm} = f(\varepsilon - \zeta_{\pm}) = (e^{(\varepsilon - \zeta_{\pm})/\kappa T} + 1)^{-1}, \quad (6.4)$$

and

$$\zeta_{\pm} = \zeta \pm \mu_B H, \quad (6.5)$$

where the suffix γ is removed and $\zeta_{\pm}$ are the chemical potentials at an effective magnetic field H . The magnetic field H is composed by an external magnetic field and the molecular field arising from the exchange interactions between electrons.

In the classical limit of high temperatures, the distribution (6.4) can be replaced by the Boltzmann distribution. If $N/V \ll (2\pi m^*/\kappa T)^{3/2}/h^3$, where the electron gas is regarded as an ideal electron gas with an effective mass m^* , we can use the distribution function, $f^{\pm} = f(\varepsilon - \zeta_{\pm}) = A \exp(-(\varepsilon \pm \mu_B H)/\kappa T)$. A is given by $N = 2A \cosh(\mu_B H/\kappa T) \int_0^{\infty} \rho(\varepsilon) \exp(-\varepsilon/\kappa T) d\varepsilon$. In the case of an ideal electron gas with an effective mass m^* , $A = (N/2V)(h^2/2\pi m^* \kappa T)^{3/2} \cdot \text{sech}(\mu_B H/\kappa T)$. From (6.2), the number of singly-occupied electrons n is $n = N - (N^2/2V) \cdot (h^2/4\pi m^* \kappa T)^{3/2} \text{sech}^2(\mu_B H/\kappa T)$. Then it can be seen that in the classical limit we can approximate as $n \approx N$.

At low temperatures where the electron gas is actually degenerate, the number of singly-occupied electrons is given in the following way. Both of f^+ and f^- are considered to be degenerate. The case where either f^+ or f^- is degenerate and the other is not degenerate will be discussed in § 8 and § 9. In the first place, the second term of the right-hand side of (6.2) is rewritten as follows:

$$\begin{aligned} 2 \int_0^{\infty} f^+ f^- \rho(\varepsilon) d\varepsilon &= -2 \int_0^{\infty} \mathcal{N}(\varepsilon) (f^+ \partial f^- / \partial \varepsilon + f^- \partial f^+ / \partial \varepsilon) d\varepsilon \\ &= 2 \sum_{n=0}^{\infty} \lambda_n (\kappa T)^n [\partial^n / \partial \zeta_-^n \{ \mathcal{N}(\zeta_-) f(\zeta_- - \zeta_+) \} + \partial^n / \partial \zeta_+^n \{ \mathcal{N}(\zeta_+) f(\zeta_+ - \zeta_-) \}], \end{aligned} \quad (6.6)$$

where $\mathcal{N}(\varepsilon) = \int_0^{\varepsilon} \rho(\varepsilon) d\varepsilon$, and $\lambda_n = (n!)^{-1} \int_{-\infty}^{\infty} \alpha^{-n} e^{-\alpha} (e^{\alpha} + 1)^2 d\alpha$. On the other hand, we have

$$N = \int_0^{\infty} (f^+ + f^-) \rho(\varepsilon) d\varepsilon = \sum_{n=0}^{\infty} \lambda_n (\kappa T)^n \{ \partial^n \mathcal{N}(\zeta_-) / \partial \zeta_-^n + \partial^n \mathcal{N}(\zeta_+) / \partial \zeta_+^n \}. \quad (6.7)$$

From (6.2), (6.6) and (6.7), n is given by

$$\begin{aligned} n &= 2 \sum_{n=0}^{\infty} \lambda_n (\kappa T)^n \left[\mathcal{N}^{(n)}(\zeta_-) \left\{ \frac{1}{2} - f(\zeta_- - \zeta_+) \right\} + \mathcal{N}^{(n)}(\zeta_+) \left\{ \frac{1}{2} - f(\zeta_+ - \zeta_-) \right\} \right] \\ &\quad - 2 \sum_{n=0}^{\infty} \sum_{m=n+1}^{\infty} \lambda_n (\kappa T)^n (n! / m! \cdot (n-m)!) [\mathcal{N}^{(m)}(\zeta_-) f^{(n-m)}(\zeta_- - \zeta_+) \\ &\quad + \mathcal{N}^{(m)}(\zeta_+) f^{(n-m)}(\zeta_+ - \zeta_-)], \end{aligned} \quad (6.8)$$

where $\mathcal{N}^{(n)}(\zeta_{\pm})$ and $f^{(n)}(\zeta_{\pm} - \zeta_{\mp})$ are n th derivatives of $\zeta_{\pm}$.

When $\mu_B H \gg \kappa T$, at low temperatures, we have $f^{(n)}(\zeta_{\mp} - \zeta_{\pm}) \propto e^{-2x}$ for $n \geq 1$, where $x = \mu_B H/\kappa T$, and from the first sum of (6.8) n is approximated as follows:

$$\begin{aligned} n_{\text{low}} &= \sum_{n=0}^{\infty} \lambda_n (\kappa T)^n \{ \mathcal{N}^{(n)}(\zeta_+) - \mathcal{N}^{(n)}(\zeta_-) \} = \mathcal{N}(\zeta_+) - \mathcal{N}(\zeta_-) + \frac{\pi^2}{6} (\kappa T)^2 \{ \mathcal{N}^{(2)}(\zeta_+) - \mathcal{N}^{(2)}(\zeta_-) \} \\ &\quad + \dots \end{aligned} \quad (6.9)$$

It is easily seen that (6.9) is the same formula for the difference between numbers of positive and negative spins, that is, $\int_0^{\infty} \rho(\varepsilon) \{ f(\varepsilon - \zeta_+) - f(\varepsilon - \zeta_-) \} d\varepsilon$. From this coincidence, it is found that the spin magnetic moments of the singly-occupied electrons cease to make any thermal

motion at low temperatures, such as $x \gg 1$, they become saturated and have the moments of μ_B respectively. The total magnetic moment of the electron gas in this case is approximately given by $n_{\text{low}}\mu_B$.

When $\mu_B H \ll \kappa T$, or $x \ll 1$, at comparatively high temperatures, by making use of the relations, $\lambda_{2m+1} = 0$, $f^{(m)}(0) = (\kappa T)^{-m} (d^m(e^x + 1)^{-1} / d\alpha^m)_{\alpha=0}$ for odd m , and $f^{(m)}(0) = 0$ for even m , n is given from the second sum of the right-hand side of (6.8) as follows:

$$n_{\text{high}} = \kappa T \{ \mathcal{N}^{(1)}(\zeta_+) + \mathcal{N}^{(1)}(\zeta_-) \} + \frac{\pi^2}{6} (\kappa T)^3 \{ \mathcal{N}^{(3)}(\zeta_+) + \mathcal{N}^{(3)}(\zeta_-) \} + \dots, \quad (6.10)$$

where the field dependence is eliminated.

Let the chemical potential at the absolute zero of temperature without the magnetic field be ζ_0 , $\zeta_0 = \varepsilon(k_0)$, and $\zeta_{\pm}$ is rewritten as $\zeta_{\pm} = \zeta_0 + \Delta\zeta \pm \mu_B H$. $\mathcal{N}(\zeta_{\pm})$, $\mathcal{N}^{(1)}(\zeta_{\pm})$, $\mathcal{N}^{(3)}(\zeta_{\pm})$, etc. are expanded in powers of κT , $\mu_B H$, and $\Delta\zeta$, as follows:

$$\begin{aligned} \mathcal{N}(\zeta_{\pm}) &= \mathcal{N}(\zeta_0) \pm \mu_B H \rho(\zeta_0) + \Delta\zeta \rho(\zeta_0) + \frac{1}{2} (\mu_B H)^2 \rho'(\zeta_0) \pm \mu_B H \Delta\zeta \rho'(\zeta_0) \pm \frac{1}{6} (\mu_B H)^3 \rho''(\zeta_0) + \dots, \\ \mathcal{N}^{(1)}(\zeta_{\pm}) &= \rho(\zeta_{\pm}) = \rho(\zeta_0) \pm \mu_B H \rho'(\zeta_0) + \Delta\zeta \rho'(\zeta_0) + \frac{1}{2} (\mu_B H)^2 \rho''(\zeta_0) + \dots, \\ \mathcal{N}^{(3)}(\zeta_{\pm}) &= \rho'(\zeta_{\pm}) = \rho'(\zeta_0) \pm \mu_B H \rho''(\zeta_0) + \dots, \end{aligned} \quad (6.11)$$

If we put (6.11) into (6.7) and use $N = 2\mathcal{N}(\zeta_0)$, $\Delta\zeta$ is given up to the powers of $(\mu_B H / \zeta_0)^2$ and $(\kappa T / \zeta_0)^2$ by,

$$\Delta\zeta = -\frac{1}{2} (\rho'(\zeta_0) / \rho(\zeta_0)) \left\{ (\mu_B H)^2 + \frac{\pi^2}{3} (\kappa T)^2 \right\}. \quad (6.12)$$

In the case where $\mu_B H \gg \kappa T$, from (6.11) n_{low} , (6.9), is rewritten as

$$n_{\text{low}} = 2\mu_B H \rho(\zeta_0) \left[1 - \frac{1}{2} (\mu_B H)^2 \left\{ \left(\frac{\rho'(\zeta_0)}{\rho(\zeta_0)} \right)^2 - \frac{1}{3} \left(\frac{\rho''(\zeta_0)}{\rho(\zeta_0)} \right) \right\} - \frac{\pi^2}{6} (\kappa T)^2 \left\{ \left(\frac{\rho'(\zeta_0)}{\rho(\zeta_0)} \right)^2 - \left(\frac{\rho''(\zeta_0)}{\rho(\zeta_0)} \right) \right\} \right]. \quad (6.13)$$

This formula is the same as the formula obtained by Stoner³⁾ for $\int_0^{\infty} \rho(\varepsilon) \{ f(\varepsilon - \zeta_+) - f(\varepsilon - \zeta_-) \} d\varepsilon$.

In the case where $\mu_B H \ll \kappa T$, from (6.11) the temperature dependence of n_{high} without the field dependence, (6.10), is written as

$$n_{\text{high}} = 2\kappa T \rho(\zeta_0) \left[1 - \frac{\pi^2}{6} (\kappa T)^2 \left\{ \left(\frac{\rho'(\zeta_0)}{\rho(\zeta_0)} \right)^2 - \left(\frac{\rho''(\zeta_0)}{\rho(\zeta_0)} \right) \right\} \right]. \quad (6.14)$$

At high temperatures such as $\mu_B H \ll \kappa T$, the spin magnetic moments of the singly-occupied electrons make violent thermal motions, and the mean magnetic moment is considered to be $\bar{\mu} = \mu_B^2 H / \kappa T$. In this case the total magnetic moment of the electron gas is given by $n_{\text{high}} \bar{\mu}$. As seen from (6.13) and (6.14), the temperature dependences of the magnetization of the electron gas are the same in the cases where $\mu_B H \gg \kappa T$ and $\mu_B H \ll \kappa T$. This can be understood from the fact that the paramagnetic moment of an ideal electron gas, in which there is no interaction between electrons, is given from (6.9), or (6.13), by n_{low} / μ_B not only in the case where $\mu_B H \gg \kappa T$, but also in the opposite case. If once the electron-electron interaction in an electron gas exists, as we must take into account its exchange interaction, the spin angular momentum of each electron is not a constant of motion, and we cannot assign the eigen-state of positive or negative spin for each electron. Therefore, Bloch's treatment¹⁾ or the calculation in this section will be useful for the present.

The one-electron energy spectrum of the electron gas having an effective mass m^* is given in the following way. According to the collective description of electron interactions by Bohm-Pines¹³⁾, as shown in § 3 and § 4, the one-electron energy of the completely degenerate

electron gas is given by $\varepsilon(\mathbf{k})$, (4.4). In the case where almost all electrons have the same direction of spin, k_c (or β) in (4.4) should be replaced by k_c' (or β') as well as k_0 is replaced by k_0' and $\varepsilon_{s,r}(\mathbf{k})$ is modified as shown in § 9. From (4.5), $\zeta_0 = \varepsilon(k_0)$ is written as

$$\zeta_0 = \zeta_F - (e^2 k_0 / \pi)(1 - \beta + \beta^2/4) + \varepsilon_{s,r}(k_0), \quad (6.15)$$

and

$$\zeta_F = \hbar^2 k_0^2 / 2m^* = 3.683 r_s^{-2} m / m^* \quad \text{in Ryd. unit.} \quad (6.16)$$

We use the relations, $\rho'(\varepsilon) = (dk/d\varepsilon)(d\rho(\varepsilon)/dk)$, and $\rho''(\varepsilon) = (dk/d\varepsilon)(d\rho'(\varepsilon)/dk)$, and from (4.4), (6.3), (6.15) and (6.16) $\rho(\zeta_0)$, $\rho'(\zeta_0)$ and $\rho''(\zeta_0)$ are given as follows:

$$\rho(\zeta_0) = 3N / (4\zeta_F C_1), \quad (6.17)$$

$$\rho'(\zeta_0) / \rho(\zeta_0) = C_2 / (2\zeta_F C_1^2), \quad (6.18)$$

$$\begin{aligned} \rho''(\zeta_0) / \rho(\zeta_0) = & -1 / (4\zeta_F^2 C_1^4) \left[1 + \lambda \left(5 \log \frac{2}{\beta} - \frac{23}{4} + 2\beta^2 \right) + \lambda^2 \left\{ -14 + \frac{133}{16} \beta^2 - \frac{5}{4} \beta^4 \right. \right. \\ & \left. \left. + \frac{85}{4} \log \frac{2}{\beta} - \frac{25}{4} \beta^2 \log \frac{2}{\beta} - 8 \left(\log \frac{2}{\beta} \right)^2 \right\} + \dots \right], \end{aligned} \quad (6.19)$$

where

$$C_1 = 1 + \lambda \left(\log \frac{2}{\beta} - 1 + \frac{\beta}{4} \right) + (m^* / \hbar^2 k_0) (d\varepsilon_{s,r} / dk)_{k=k_0}, \quad (6.20)$$

$$C_2 = 1 + \lambda \left(3 \log \frac{2}{\beta} - \frac{7}{2} + \beta^2 \right) + (m^* / \hbar^2) \{ (2/k) d\varepsilon_{s,r} / dk - d^2 \varepsilon_{s,r} / dk^2 \}_{k=k_0}, \quad (6.21)$$

and $\lambda = e^2 m^* / \pi \hbar^2 k_0 = \pi^{-1} (9\pi/4)^{-1/3} (m^*/m) r_s = 0.1659 r_s (m^*/m)$. In $\rho''(\zeta_0)$, (6.19), we have omitted to write the term due to the short-range correlation, $\varepsilon_{s,r}$, for the sake of simplicity.

From (6.17), (6.18) and (6.19), (6.13) and (6.14) are written, respectively, as

$$n_{\text{low}} = \frac{3\mu_B H N}{2\zeta_F C_1} \left\{ 1 - \frac{(\mu_B H)^2}{8\zeta_F^2} C' - \frac{\pi^2 (\kappa T)^2}{24\zeta_F^3} C' \right\}, \quad (6.22)$$

$$n_{\text{high}} = \frac{3\kappa T N}{2\zeta_F C_1} \left\{ 1 - \frac{\pi^2 (\kappa T)^2}{24\zeta_F^3} C' \right\}, \quad (6.23)$$

where

$$\begin{aligned} C' = 2C_1^{-1} \left[1 + \lambda \left(\frac{11}{2} \log \frac{2}{\beta} - \frac{51}{8} + 2\beta^2 \right) + \lambda^2 \left\{ -\frac{7}{8} + \frac{21}{32} \beta^2 - \frac{1}{8} \beta^4 + \frac{1}{8} \log \frac{2}{\beta} \right. \right. \\ \left. \left. - \frac{1}{8} \beta^2 \log \frac{2}{\beta} + \frac{1}{2} \left(\log \frac{2}{\beta} \right)^2 \right\} + \dots \right], \end{aligned} \quad (6.24)$$

$$\begin{aligned} C'' = \frac{4}{3} C_1^{-1} \left[1 + \lambda \left(\frac{23}{4} \log \frac{2}{\beta} - \frac{107}{16} + 2\beta^2 \right) + \lambda^2 \left\{ \frac{91}{16} - \frac{203}{64} \beta^2 + \frac{7}{16} \beta^4 - \frac{167}{16} \log \frac{2}{\beta} \right. \right. \\ \left. \left. + \frac{47}{16} \beta^2 \log \frac{2}{\beta} + \frac{19}{4} \left(\log \frac{2}{\beta} \right)^2 \right\} + \dots \right]. \end{aligned} \quad (6.25)$$

The terms due to short-range correlation, $\varepsilon_{s,r}(\mathbf{k})$, in C' and C'' have been omitted as they have been in (6.19). When the one-electron energy $\varepsilon(\mathbf{k})$ is given only by the first term, $\varepsilon_K(\mathbf{k})$, of the right-hand side of (4.4), that is, the electron gas is ideal, it is easily found that $C_1 = C_2 = 1$, $C' = 2$, and $C'' = 4/3$.

§ 7. Ferromagnetic Properties of an Electron Gas: The Curie Temperature and the Susceptibilities above the Curie Point

First we consider the case at high temperatures, so that the electron gas is in the non-

degenerate state. As mentioned before, at high temperatures the thermal excitation of electrons becomes remarkable, the probability that each state is occupied by an electron is small, and all electrons can be regarded to occupy the states singly. Then from (2.4) and $g=2$ the mean magnetic moment is $M=N\mu_B \tanh \{ \mu_B(H+\alpha M)/\kappa T \}$. This is the same expression as the one obtained from the classical point of view. It should be noted that the coefficient of the molecular field α is not given by (4.11) or (4.16), but is given by the average of the exchange fields over the Boltzmann distribution. At high temperatures, we have $M=N\mu_B^2(H_0+\alpha M)/\kappa T$, and the susceptibility shows the Curie-Weiss law such as,

$$\chi = C/(T - \theta_p), \quad (7.1)$$

where

$$C = N\mu_B^2/\kappa, \quad (7.2)$$

$$\theta_p = N\mu_B^2\alpha/\kappa. \quad (7.3)$$

Secondly we consider the case where the electron gas is in the degenerate state. From (2.4) and $g=2$, the magnetization of the electron gas is given by

$$M = n\mu_B \tanh \{ \mu_B(H_0 + \alpha M)/\kappa T \}, \quad (7.4)$$

where n is given by (6.8). Above the Curie temperature the condition, $\mu_B H = \mu_B(H_0 + \alpha M) < \kappa T$, holds, and we must use n_{high} , (6.23), for n in (7.4). We expand (7.4) as follows:

$$M = n\mu_B^2(H_0 + \alpha M)/\kappa T. \quad (7.5)$$

From (6.23) and (7.5),

$$M = (H_0 + \alpha M)(3N\mu_B^2/2\zeta_F C_1) \left\{ 1 - \frac{\pi^2}{24} (\kappa T/\zeta_F)^2 C' \right\}. \quad (7.6)$$

In order that a finite value of M may be a solution of (7.6) when $H_0=0$, there must be the Curie temperature T_c which satisfies the following equation, $1 = (3N\mu_B^2\alpha/2\zeta_F C_1) \{ 1 - (\pi^2/24) \cdot (\kappa T_c/\zeta_F)^2 C' \}$, and we obtain

$$T_c = \frac{\sqrt{24}\zeta_F}{\pi\kappa} (C')^{-1/2} \left\{ 1 - \frac{2\zeta_F C_1}{3N\mu_B^2\alpha} \right\}^{1/2}. \quad (7.7)$$

In order that T_c is real, it must hold that $1 - (2\zeta_F C_1/3N\mu_B^2\alpha) > 0$. From the approximations $\varepsilon_{s,r} \approx \varepsilon_{s,r}^a$ at larger r_s ($5 > r_s > 2$), and $\varepsilon_{s,r} \approx 2\varepsilon_{s,r}^a$ at smaller r_s ($r_s < 2$)¹⁶⁾ and from (3.2), (4.11), (6.16) and (6.20), the relations between r_s and m^*/m at larger and smaller r_s which satisfy $1 - (2\zeta_F C_1/3N\mu_B^2\alpha) = 0$, are shown in Fig. 1 by curves (6) and (7) respectively. The crossing of curves (1) and (6) or (7) is due to the difference of their approximations. For the electron gas having the values of r_s and m^*/m in the region between curves (1) and (6) the state in which only a part of all electron spins are parallel is expected to be stable in energy at the absolute zero of temperature.

From (7.6) and (7.7) the susceptibility above the Curie temperature is obtained as

$$1/\chi = H_0/M = \alpha \left[1 - \left(\frac{3N\mu_B^2\alpha}{2\zeta_F C_1} - 1 \right) \left(\frac{T^2}{T_c^2} - 1 \right) \right]^{-1} - \alpha. \quad (7.8)$$

If $\kappa T_c \ll \zeta_F$, from (7.7) we can consider that $3N\mu_B^2\alpha/(2\zeta_F C_1) \approx 1$. In this case (7.8) can be approximated in the neighbourhood of the Curie temperature as follows:

$$1/\chi = \xi \{ (T/T_c)^2 - 1 \}, \quad (7.9)$$

$$\xi = \alpha \{ (3N\mu_B^2\alpha/2\zeta_F C_1) - 1 \}. \quad (7.10)$$

On the other hand, if $\kappa T_c \gg \zeta_F$, the electron gas is not in a degenerate state above the

Curie temperature and the susceptibility ought to show the Curie-Weiss law, (7.1), (7.2) and (7.3). In the intermediate case the number of electrons occupying levels singly will be determined as a function of temperature by the following way. $f(\varepsilon - \zeta_{\pm})$ is expanded in powers of H as, $f(\varepsilon - \zeta_{\pm}) = (f(\varepsilon - \zeta))_{H=0} \pm \mu_B H (\partial f(\varepsilon - \zeta) / \partial \zeta)_{H=0} + O(H^2)$. Putting this into (6.2), we have at $H=0$,

$$n \equiv n(T) = -2 \int_0^{\infty} (f(\varepsilon - \rho))_{H=0}^2 \rho(\varepsilon) d\varepsilon. \quad (7.11)$$

As the magnetization M above the Curie temperature is approximated as (7.5), in order that $M \approx 0$ may be a solution of (7.5) with (7.11), there must be the Curie temperature which satisfies $(\kappa T_c / \mu_B)^{-2} (n(T_c) - \alpha) = 0$. The susceptibility above the Curie temperature in this case is given by

$$1/\chi = H_0/M = \kappa T \mu_B^2 / n(T) - \alpha. \quad (7.12)$$

In the case where $\kappa T_c \approx \zeta_F$, there is no way but to do numerical calculations in order to find the temperature dependence of $n(T)$.

In conclusion, the variation with temperature of the susceptibility of a ferromagnetic electron gas is given by (7.9) in the neighbourhood of the Curie temperature and is expected to be the Curie-Weiss law at temperature higher than the degeneracy temperature when the Curie temperature is much lower than the degeneracy temperature. When the Curie temperature is comparable to the degeneracy temperature, the variation with temperature of the susceptibility in the neighbourhood of T_c will be obtained by numerical calculations. It seems to be very difficult to do these numerical calculations actually because of the complexity of the level density given by (4.4) and (6.3). It is qualitatively understood from (7.12) that curve $1/\chi$ versus T is concave down-wards and χ follows the Curie-Weiss law above the degeneracy temperature.

Finally, in the case where the Curie temperature does not exist, namely in the case where the electron gas has the values of r_s and m^*/m , which are found in the lower region of curve 6) or (7), and is not ferromagnetic at any temperature, the paramagnetic susceptibility when $\kappa T \ll \zeta_F$ is written from (7.6) as,

$$\frac{1}{\chi} = \frac{1}{\chi_0} + \eta T^2, \quad (7.13)$$

where

$$1/\chi_0 = (2\zeta_F C_1 / 3N\mu_B^2) - \alpha, \quad (7.14)$$

$$\eta = (\pi^2 \kappa^2 C_1 C' / 36\mu_B^2 \zeta_F). \quad (7.15)$$

As the electron gas at present is not ferromagnetic, it is seen that $1/\chi_0$ is positive. From 7.13 curve of $1/\chi$ versus T is concave upwards when $\eta > 0$ and apparently it seems to be antiferromagnetic. As shown in § 10, the variations with temperature of the paramagnetic susceptibilities for γ -Fe, Pd and Pt at comparatively higher temperature is well expressed by the formula (7.13). Stoner²³⁾ has already shown that χ , instead of $1/\chi$, is expressed as the sum of a constant and the term proportional to T^2 .

§ 8. Spin-Wave Motion in an Electron Gas

When the magnetic field H is applied to an electron gas and $\mu_B H \gg \kappa T$, the number of singly-occupied electrons in the neighbourhood of the Fermi surface, n , is given by (6.22). In § 6 it has been shown that n_{low} is equal to the difference between the numbers of electrons with positive and negative spins. This fact means that at low temperatures there is scarcely any thermal motion of spins of the singly-occupied electrons and the component of the mean magnetic moment of an electron along the magnetic field is nearly equal to μ_B . We suppose that the levels with wave vectors between k_+ and k_- are singly and compactly

occupied by electrons and the levels below k_- are doubly occupied by electrons. We regard these singly-occupied electrons as magnetic carriers.

It is well-known that the eigen-states of the spin-wave are easily found so long as the magnetic electrons (or carriers) are localized on certain lattice points. Using the atomic functions Slater⁸⁾ has studied the spin-wave theory of itinerant electrons. The theory has been applied only to insulators in which the procedure used by Slater is strictly correct. In conductors such as monovalent metals, if we can localize the itinerant electrons on lattice points we can easily study the spin-wave motion of the localized electrons. But to discuss the cohesive energy of metals, the approximation of using localized electrons will be undoubtedly unsatisfactory. It follows that the singly-occupied electrons are magnetic carriers and will be described by localized wave functions in a fairly good approximation as they are mostly not concerned with cohesion; and the doubly-occupied electrons will mainly contribute to the cohesive forces in metals.

We make the localized orbits from the plane waves with wave vectors between k_+ and k_- in the following way. We use the same method as when the atomic functions are constructed from the Bloch functions. Herring¹⁰⁾ used this method in the rough calculation of the Bloch wall coefficient. In a volume of electron gas, we imagine n lattice points. Let the lattice be a simple cubic lattice tentatively. It will soon be found that the final result does not depend on the type of the lattice structure. Let the co-ordinates of the lattice points be $\mathbf{R}$. From the wave function of a free electron with wave vector $\mathbf{k}$, $\varphi_{\mathbf{k}}(\mathbf{r}) = (1/V)^{1/2} \cdot e^{i\mathbf{k} \cdot \mathbf{r}}$, we construct the following functions, $\psi(\mathbf{r} - \mathbf{R})$,

$$\psi(\mathbf{r} - \mathbf{R}) = (1/n)^{1/2} \sum_{k_- < k < k_+} e^{-i\mathbf{k} \cdot \mathbf{R}} \varphi_{\mathbf{k}}(\mathbf{r}), \quad (8.1)$$

where the sum is taken over n states with the wave vectors between k_+ and k_- . When the number of the singly-occupied electrons is far less than the total number of electrons, that is, $n \ll N$, we find, on changing the sum to integral, and using (3.8),

$$\psi(\mathbf{r} - \mathbf{R}) = (n/V)^{1/2} \sin(k_0 |\mathbf{r} - \mathbf{R}|) / (k_0 |\mathbf{r} - \mathbf{R}|). \quad (8.2)$$

An overlap integral between the orbits localized at $\mathbf{R}$ and $\mathbf{R}'$ is

$$\int \psi^*(\mathbf{r} - \mathbf{R}) \psi(\mathbf{r} - \mathbf{R}') d\mathbf{r} = \sin(k_0 |\mathbf{R} - \mathbf{R}'|) / (k_0 |\mathbf{R} - \mathbf{R}'|). \quad (8.3)$$

As $\mathbf{R}$ and $\mathbf{R}'$ are the lattice points having a lattice spacing of about $(V/n)^{1/3}$, $|\mathbf{R} - \mathbf{R}'| k_0 \geq (V/n)^{1/3} k_0 = (3\pi^2 N/n)^{1/3}$. When $n \ll N$, $|\mathbf{R} - \mathbf{R}'| k_0 \gg \pi$, and we can consider that the overlap integral (8.3) vanishes approximately. Then it may be assumed that the localized orbits (8.1) are orthogonal with one another. Strictly speaking, as the orbit $\psi(\mathbf{r} - \mathbf{R})$ is not orthogonal with others, correction due to non-orthogonality is necessary when the vector model is adopted. The first-order correction to the exchange integral is the order of the magnitude of the product of the Coulomb integral and the square of the overlap integrals²¹⁾. As seen from (3.1), the interactions between electrons are short-range, so that the value of the Coulomb integral will not be large, and we shall be able to neglect the correction. In the Appendix it will be shown that when $n \ll N$ the correction due to non-orthogonality may be practically ignored.

When $n = N$, namely all electrons singly occupy all levels with wave vectors up to k_0' , we make the following functions:

$$\psi(\mathbf{r} - \mathbf{R}) = N^{-1/2} \sum_{0 < k < k_0'} e^{-i\mathbf{k} \cdot \mathbf{R}} \varphi_{\mathbf{k}}(\mathbf{r}) = \frac{N}{V} \frac{3}{k_0'^3 |\mathbf{r} - \mathbf{R}|^3} \{ \sin(k_0' |\mathbf{r} - \mathbf{R}|) - k_0' |\mathbf{r} - \mathbf{R}| \cos(k_0' |\mathbf{r} - \mathbf{R}|) \}, \quad (8.4)$$

where the relation $V k_0'^3 = 6\pi^2 N$ is made use of. An overlap integral between the orbits localized at $\mathbf{R}$ and $\mathbf{R}'$ is

$$\int \psi^*(\mathbf{r} - \mathbf{R}) \psi(\mathbf{r} - \mathbf{R}') d\mathbf{r} = 3 k_0'^{-3} |\mathbf{R} - \mathbf{R}'|^{-3} \{ \sin(k_0' |\mathbf{R} - \mathbf{R}'|) - k_0' |\mathbf{R} - \mathbf{R}'| \cos(k_0' |\mathbf{R} - \mathbf{R}'|) \}. \quad (8.5)$$

The degree of the non-orthogonality in (8.5) is larger than that in (8.3). As shown in the Appendix, the correction of non-orthogonality in the exchange integral even in this case, $n = N$, is not so large, so that here we treat the wave functions (8.4) as if they were orthogonal with one another.

The exchange integral between the orbits localized at $\mathbf{R}$ and $\mathbf{R}'$ is written as

$$J_{\mathbf{R}\mathbf{R}'} = \iint \phi^*(\mathbf{r}_1 - \mathbf{R}) \phi^*(\mathbf{r}_2 - \mathbf{R}') v(\mathbf{r}_1 - \mathbf{r}_2) \phi(\mathbf{r}_1 - \mathbf{R}') \phi(\mathbf{r}_2 - \mathbf{R}) d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.6)$$

where $v(\mathbf{r}_1 - \mathbf{r}_2)$ is the effective potential energy between the electrons 1 and 2. From (3.5), (4.5) and (4.6) the Fourier components of $v(\mathbf{r}_1 - \mathbf{r}_2)$ is given by

$$v(\mathbf{k}' - \mathbf{k}) = J_{\mathbf{k}\mathbf{k}'}^{s,c} + J_{\mathbf{k}\mathbf{k}'}^{s,r} + J_{\mathbf{k}\mathbf{k}'}^{r,p} = V^{-2} \iint e^{-i(\mathbf{k} \cdot \mathbf{r}_1 + \mathbf{k}' \cdot \mathbf{r}_2)} v(\mathbf{r}_1 - \mathbf{r}_2) e^{i(\mathbf{k}' \cdot \mathbf{r}_1 + \mathbf{k} \cdot \mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2 = V^{-1} \int e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} v(\mathbf{r}) d\mathbf{r}. \quad (8.7)$$

Introducing (8.1) into (8.6), we have

$$J_{\mathbf{R}\mathbf{R}'} = n^{-2} \sum_{\mathbf{k}} v(\mathbf{k}) \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} e^{i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}) \cdot (\mathbf{R} - \mathbf{R}')}, \quad (8.8)$$

where the sums over $\mathbf{k}_1$ and $\mathbf{k}_2$ are restricted to the regions, $k_- < k_1 < k_+$, $k_- < k_2 < k_+$, $k_- < |\mathbf{k}_1 - \mathbf{k}| < k_+$, and $k_- < |\mathbf{k}_2 + \mathbf{k}| < k_+$. When $n = N$, $J_{\mathbf{R}\mathbf{R}'}$ is given by a formula similar to that in (8.8) if in (8.8) n , k_+ and k_- are replaced by N , k_0' and 0, respectively.

When the n localized orbits are all occupied by electrons singly, the exchange energy is

$$- \frac{1}{2} \sum_{i>j} (1 + 4\mathbf{s}_i \cdot \mathbf{s}_j) J_{\mathbf{R}_i \mathbf{R}_j}, \quad (8.9)$$

where $\mathbf{s}_i$ and $\mathbf{s}_j$ are the spin operators of electrons localized at $\mathbf{R}_i$ and $\mathbf{R}_j$ respectively. In order to take out the mode of the spin-wave motion, we make use of the Holstein and Primakoff method⁷⁾. After the well-known transformations of (8.9) we have for (8.9)

$$\mathcal{H} = \sum_{\lambda} A_{\lambda} a_{\lambda}^* a_{\lambda}, \quad (8.10)$$

$$A_{\lambda} = \sum_{\mathbf{h}} J_{\mathbf{R}\mathbf{h}} \{1 - \exp(i\mathbf{K}_{\lambda} \cdot \mathbf{R}_{\mathbf{h}})\}, \quad (8.11)$$

where $J_{\mathbf{R}\mathbf{h}}$ is $J_{\mathbf{R}\mathbf{R}'}$ in (8.8) when $\mathbf{R} - \mathbf{R}' = \mathbf{R}_{\mathbf{h}}$, and a_{λ} and a_{λ}^* satisfy the relation, $a_{\lambda} a_{\lambda'}^* - a_{\lambda'}^* a_{\lambda} = -\delta_{\lambda\lambda'}$. From the well-known Born-von Karman periodic boundary conditions, components of $\mathbf{K}_{\lambda}$ are required to take the values, $K_{\lambda}^x = 2\pi\lambda_x/aL_x$, $K_{\lambda}^y = 2\pi\lambda_y/aL_y$, $K_{\lambda}^z = 2\pi\lambda_z/aL_z$, where L_x , L_y , L_z are the lengths of the box, which contains the electron gas, in x , y , z directions, divided by the lattice spacing, a , and λ_x , λ_y , λ_z are any integral values between $-\frac{1}{2}L_x$ and $\frac{1}{2}L_x - 1$, $-\frac{1}{2}L_y$ and $\frac{1}{2}L_y - 1$, $-\frac{1}{2}L_z$ and $\frac{1}{2}L_z - 1$, respectively.

From (8.8), A_{λ} becomes

$$A_{\lambda} = n^{-1} \left\{ \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} v(\mathbf{k}_1 - \mathbf{k}_2) - \sum'_{\mathbf{k}_1} \sum'_{\mathbf{k}_2} v(\mathbf{k}_1 - \mathbf{k}_2) \right\}, \quad (8.12)$$

where the regions of the sums are specified by $k_- < k_1 < k_+$ and $k_- < k_2 < k_+$ in the first term, and $k_- < k_1 < k_+$, $k_- < k_2 < k_+$, $k_- < |\mathbf{k}_1 + \mathbf{K}_{\lambda}| < k_+$, and $k_- < |\mathbf{k}_2 + \mathbf{K}_{\lambda}| < k_+$ in the second term. On changing the sums to integrals, the necessary integrations of the second term in (8.12) have not been carried out. Then we replace the integrand in the second term by the mean of the integrand in the first term, in order to evaluate the second term. When $n \ll N$ and $K_{\lambda} \ll k_+ - k_- \ll k_0$, we approximately find

$$A_{\lambda} = n^{-1} (3NK_{\lambda}/4k_0n)^2 \sum_{k_- < k_1 < k_+, k_- < k_2 < k_+} v(\mathbf{k}_1 - \mathbf{k}_2). \quad (8.13)$$

When $n = N$ and $K_{\lambda} \ll k_0'$, we have also

$$A_{\lambda}^N = N^{-1} (3K_{\lambda}/4k_0')^2 \sum_{0 < k_1 < k_0'} \sum_{0 < k_2 < k_0'} v(\mathbf{k}_1 - \mathbf{k}_2). \quad (8.14)$$

(8.13) can be rewritten, from (2.5), (4.11) and (8.7), as follows:

$$A_{\lambda} = AK_{\lambda}^2, \quad (8.15)$$

$$A = (9N^2 \mu_B^2 / 8k_0^2 n) \alpha. \quad (8.16)$$

Similarly (8.14) can be rewritten, from (2.5), (4.16) and (8.7), as follows:

$$A_{\lambda}^N = A_N K_{\lambda}^2, \quad (8.17)$$

$$A_N = (9N \mu_B^2 / 8k_0'^2) \alpha_N. \quad (8.18)$$

As eigen values of $n_{\lambda} = a_{\lambda}^* a_{\lambda}$ are positive integers, 0, 1, 2, ..., the mean value of n_{λ} becomes,

$$\bar{n}_{\lambda} = \{\exp(A_{\lambda}/\kappa T) - 1\}^{-1}, \quad \text{or} \quad \bar{n}_{\lambda} = \{\exp(A_{\lambda}^N/\kappa T) - 1\}^{-1}. \quad (8.19)$$

The magnetization along z direction is given by

$$M = 2\mu_B \langle \sum_i s_i^z \rangle_{AV} = 2\mu_B \left(\frac{1}{2} n - \sum_{\lambda} \bar{n}_{\lambda} \right). \quad (8.20)$$

When $n \ll N$, from (8.15), (8.16) and (8.19) we use the well-known procedure and obtain

$$\sum_{\lambda} \bar{n}_{\lambda} = 2.315 (V/4\pi^2) (\kappa T/A)^{3/2}, \quad (8.21)$$

and

$$M = \mu_B n \{1 - \delta(n/N)^{1/2} T^{3/2}\}, \quad (8.22)$$

$$\delta = 4.639 \times 10^{-8} (2a_0 N \mu_B^2 e^{-2} \alpha)^{-3/2} (\text{°K})^{-3/2}. \quad (8.23)$$

When $n \approx N$, from (8.17), (8.18), (8.20) and (8.21) we have,

$$M = \mu_B n (1 - \delta_N T^{3/2}), \quad (8.24)$$

$$\delta_N = 9.279 \times 10^{-8} (2a_0 N \mu_B^2 e^{-2} \alpha_N)^{-3/2} (\text{°K})^{-3/2}. \quad (8.25)$$

At low temperatures n is given by (6.22). From (6.22) and (8.22) we can find the variations with temperature of n_{low} and M . Putting $H_0 = 0$ and $H = \alpha M$ and using the approximation,

$H = \alpha M = \alpha \mu_B n_{\text{low}}$, in (6.22), we have

$$n_{\text{low}} = (3\mu_B^2 N \alpha n_{\text{low}} / 2\zeta_F C_1) \left\{ 1 - \frac{1}{8} (\alpha \mu_B n_{\text{low}} / \zeta_F)^2 C'' - \frac{1}{24} (\pi \kappa T / \zeta_F)^2 C' \right\}. \quad (8.26)$$

As $n_{\text{low}} \rightarrow 0$, it must hold that $1 = (3\mu_B^2 N \alpha / 2\zeta_F C_1) \left\{ 1 - \frac{1}{8} (\alpha \mu_B n_{\text{low}} / \zeta_F)^2 C'' - \frac{1}{24} (\pi \kappa T / \zeta_F)^2 C' \right\}$.

From the condition, T_c is real, we can easily see that the solution of this exists, and the solution is

$$n/N = m_0 (1 - \delta_2 T^2), \quad (8.27)$$

$$m_0 = (24 \alpha \mu_B^2 N / \zeta_F - 16 C_1)^{1/2} (3C'')^{-1/2} (\alpha \mu_B^2 N / \zeta_F)^{-3/2}, \quad (8.28)$$

$$\delta_2 = (\pi/4)^2 \kappa^2 \zeta_F^{-2} \alpha \mu_B^2 N C' / (3 \alpha \mu_B^2 N - 2 \zeta_F C_1). \quad (8.29)$$

From (8.22) and (8.27) we have for the magnetization at low temperatures,

$$M/(N \mu_B) = m_0 (1 - \delta_{3/2} T^{3/2} - \delta_2 T^2), \quad (8.30)$$

where

$$\delta_{3/2} = \delta m_0^{1/2}, \quad (8.31)$$

and $N\mu_B m_0$ is spontaneous magnetization at 0°K . It may happen that m_0 in (8.28) is larger than one. It is due to the fact that n/N is approximately obtained in powers of $\mu_B H/\zeta_F$ and $\kappa T/\zeta_F$, and as it is meaningless that $m_0 > 1$, we may put $m_0 = 1$ in this case.

When $n \approx N$, the coefficient of the molecular field α_N is given by (4.16) and we have

$$n/N = m_{0N}(1 - \delta_2^N T^2), \quad (8.32)$$

$$m_{0N} = (24\alpha_N \mu_B^2 N / \zeta_F - 16C_1)^{1/2} (3C')^{-1/2} (\alpha_N \mu_B^2 N / \zeta_F)^{-3/2}, \quad (8.33)$$

$$\delta_2^N = (\pi/4)^2 (\kappa/\zeta_F)^2 \alpha_N \mu_B^2 N C' / (3\alpha_N \mu_B^2 N - 2C_1 \zeta_F). \quad (8.34)$$

From (8.24) and (8.32) the magnetization is given by

$$M/(N\mu_B) = m_{0N}(1 - \delta_{3/2}^N T^{3/2} - \delta_2^N T^2), \quad (8.35)$$

where $\delta_{3/2}^N = \delta_N$.

It should be noted that when $n = N$ and either the distribution function f^+ of f^- is degenerate and the other is not degenerate, the approach of n to N is exponential and we should not use (8.32), in which both the f^+ and f^- are assumed to be degenerate, to obtain the temperature dependence of magnetization. Instead of (8.35) we have in this case,

$$M/(N\mu_B) \approx 1 - \delta_{3/2}^N T^{3/2}, \quad (8.36)$$

and the term proportional to T^2 does not appear.

As seen easily from (7.7), (8.29) and (8.34) there is the following relation between T_c and δ_2 or δ_2^N ,

$$T_c^2 \delta_2 = \frac{1}{2}, \quad \text{or} \quad T_c^2 \delta_2^N = \frac{1}{2}. \quad (8.37)$$

§ 9. Comparisons with the Experimental Results of Ferromagnetic Transition Metals

In § 7 and § 8 we have derived the formulas for the Curie temperature, and the variations with temperature of spontaneous magnetization and susceptibility above the Curie point as the functions of r_s and m^*/m , respectively, when an electron gas shows ferromagnetism. In this section, we shall make a comparison between the above results of an electron gas and the experimental results of ferromagnetic transition metals. It may not be a good approximation to say that the magnetic electrons in the transition metal are treated as if they construct an electron gas. Namely, many discussions claiming that the localized model for magnetic electrons is the better approximation have been so far presented²²⁾, and the experimental supports of this model have been found from the experiments of the neutron diffraction²³⁾ and X-ray diffraction²⁴⁾, although there are a few opposite views on

the latter experiment²⁵⁾. The model in which the magnetic electrons are localized in Fe has been specially proposed²⁶⁾. However, it is certain that there is a translational motion, (which is the main motion in gas), in the transition metals including Fe, because at low temperatures the large specific heats proportional to T are observed for the transition metals. Then it will be useful to adopt the model of an electron gas for the magnetic electrons in the transition metals, and we can see whether the model is valid or not by comparing its magnetism with the experimental results of ferromagnetic transition metals. At any rate, Bloch's itinerant one-electron wave functions are eigen functions in crystal, but there are two ways in the treatment of the correlation due to the Coulomb interaction, that is, the strong correlation where the Heitler-London model or atomic model is used and the weak correlation where the band model or the electron gas model is used. In this paper we assume the latter

Table I. Crystal structure, lattice constant²⁷⁾, number of electrons or positive holes per atom p , electron mean distance r_s , effective mass m^* .

Element	Crystal structure	Lattice constant Å	Number of electrons or positive holes p	r_s at. u.	m^*/m (free)	m^*/m
Ni	f.c.c.	3.5167	10	1.2055	7.10	3.76
Co	h.c.p.	2.502=a 4.061=c	9	1.246	5.14	3.08
Co	f.c.c.	3.5368	9	1.2557	5.02	3.02
Fe	b.c.c.	2.8606	8	1.3309	5.02	2.94
Mn	Cubic	8.897	7	1.409	14.1	4.35
Cr	b.c.c.	2.8787	6	1.4741	1.73	1.36
Ni	f.c.c.	3.5167	0.6	3.0793	28.8	3.44
Co	h.c.p.	2.502=a 4.061=c	1.7	2.172	13.3	4.15
Co	f.c.c.	3.5368	1.7	2.1886	13.1	4.12
Fe	b.c.c.	2.8606	2.2	2.0466	12.3	4.24

model for the $3d$ electrons in transition metals and take into account the effect of the correlation on the itinerant model correctly as possible.

We determine r_s from the lattice constants and m^*/m so as to explain the electronic specific heats at low temperatures in the following way. In the first place, to determine r_s there are two ways. We have so far treated an ensemble of N electrons. It is assumed that N electrons are the valence electrons taken out from atoms. The value of r_s depends upon the number of valence electrons per atom. On the one hand we assume that the electron gas is made up of all the electrons which are $3d$ and $4s$ electrons in the atomic state. Let the number of electrons per atom be p , p is given by 10 for Ni, 9 for Co, and 8 for Fe. In the upper half of Table I we have given the crystal structures, the lattice

constants²⁷⁾, the numbers of valence electrons per atom, p , and r_s , of not only Ni, Co and Fe but also Mn and Cr. In this model, it will be expected that only a small part of the electrons on the Fermi surface contribute to magnetism, and the coefficient of the molecular field is given by α , (4.11). The distribution of electrons at 0°K in this case is shown in Fig. 3(a).

On the other hand, as it is well-known, the numbers of the Bohr magneton of spontaneous magnetizations in Ni, Co and Fe are explained to be equal to the numbers of positive holes in the $3d$ bands. Therefore, we take the gas of the positive holes having an effective mass m^* instead of the electron gas. The number of the positive holes per atom p is determined to be the number of the Bohr magneton per atom. Namely, p is 0.6 for Ni, 1.7 for Co, and 2.2 for Fe. Using these values of p , we gives the values of r_s for the positive hole gas in the lower half of Table I. In this case almost all the positive holes are considered to be magnetic carriers, that is, to occupy singly,* and the coefficient of the molecular field is given by α_N , (4.16).

* In Co and Fe, it may be thought that the positive holes with both positive and negative spins exist at $T=0^\circ\text{K}$ instead of the distribution shown in Fig. 3(b). r_s in this case become smaller than the values given in Table I. For the sake of simplicity we consider only the case given in the text and it is expected that both cases are not so different either qualitatively or quantitatively.

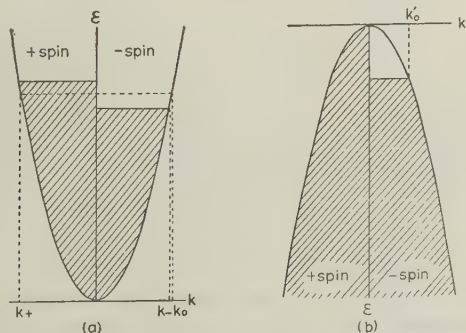


Fig. 3. Two models of electron gas: (a) real electron gas, (b) positive hole gas.

The distribution of electrons, or positive holes, at $T=0^\circ\text{K}$ in this case is shown in Fig. 3(b).

When we consider the positive holes gas, it may be question that the screening distance $1/k_0$ of the electron interaction is determined from the relation, $\beta' = k_0'/k_0' = 0.30r_s^{1/2}$, in which r_s is related only to the positive hole density. It is best for k_0' to be determined experimentally, but at present such experiments on Ni, Co and Fe have not yet been performed.¹³⁾ Accordingly, we assume that the positive hole gas is constructed from p positive holes per atom, the positive holes have the effective mass m^* , and the positive hole gas is treated quite as well as the electron gas having the same effective mass except that the positive hole has a charge of the opposite sign to the charge of electrons. In other words, the above assumption is equivalent to what we consider only the electrons which occupy singly at the upper part of the distribution shown in Fig. 3(b). It is assumed that k_0' is always determined from $\beta' = 0.30r_s^{1/2}$ in the case of the larger magnetization of the positive hole gas at lower temperatures, where r_s is related only to the positive hole density, (or the electron density). But in the neighbourhood of and above the Curie temperature the net magnetization per electron becomes small and we use the k_0 given by (3.2) for the sake of simplicity as mentioned before.

In the case shown in Fig. 3(b), it must be realized that $2\mu_B H \geq \zeta_0'$, where ζ_0' is the energy of the positive hole in the Fermi surface at $T=0^\circ\text{K}$, and H is a resultant magnetic field of an external field H_0 and the molecular field $\alpha_N M$. When $2\mu_B H \geq \zeta_0'$ at the absolute zero of temperature all the positive holes have the same direction of spins. Therefore the distribution of either f^+ or f^- is degenerate, so that, as mentioned above, from the simple calculation we can find that the effective number of the electrons, or the positive holes, which are magnetic carriers is nearly equal to the total number of the electrons, or the positive holes, in the neighbourhood of the absolute zero of temperature and this number decreases exponentially, $\exp(-2\mu_B H/\kappa T)$, as the temperature rises. At lower temperatures, we may put $n=N$, and it is expected that the variation with

temperature of spontaneous magnetization will fairly well follow $T^{3/2}$ law. And in the neighbourhood of the Curie temperature $M \approx 0$ and $\mu_B H < \kappa T$, so n will be given by n_{high} , (6.23), as long as the positive hole gas is yet degenerate. In this case, the distribution of electrons at low temperatures is the one shown in Fig. 3(b), and at higher temperatures will be the one shown in Fig. 3(a). Therefore, the coefficient of the molecular field is expected to change with temperature and may be given by α_N , (4.16), at lower temperatures, but by α , (4.11), at higher temperatures. As seen from the above discussions, in the case where all the spins of the positive holes, or the electrons, are parallel at 0°K , as shown in Fig. 3(b), the temperature dependence of the magnetization at low temperatures will be better expressed by (8.36) rather than (8.35) and that in the neighbourhood of the Curie temperature will be given by (6.23) and (7.4) with α in (4.11).

In the second place, we determine the effective mass m^* of the electron, or the positive hole, so as to explain the observed low temperature electronic heat coefficient. The low temperature electronic specific heat per electron when the number of positive spins is nearly equal to that of negative spins at 0°K , as in Fig. 3(a), is given by

$$C_e = \frac{2\pi^2 \kappa^2 T}{3N} \rho(\zeta_0) = \frac{\pi^2 \kappa^2 T}{k_0 (d\varepsilon/dk)_{k=k_0}} = \gamma T, \quad (9.1)$$

where $\rho(\zeta_0)$ is given by (6.17). The specific heat per atom is p times as large as (9.1). As r_s is comparatively small in this case (cf. Table I), $\varepsilon_{s,r}^p$ in (4.3) is approximately equal to $\varepsilon_{s,r}^a$, and we take $\varepsilon_{s,r} = \varepsilon_{s,r}^a + \varepsilon_{s,r}^p = 2\varepsilon_{s,r}^a$ in (4.4). With the aid of Fletcher and Larson's calculations on $(d\varepsilon_{s,r}^a/dk)_{k=k_0}^{16)}$, and the observed values of γ in (9.1), the effective masses m^* for model (a) are determined from (6.17), (6.20) and (9.1), and the values for Ni, Co, Fe, Mn and Cr are given in the seventh column of the upper half of Table I and are indicated by circles in Fig. 1. It is seen from Fig. 1 that Cr is never ferromagnetic, but in Mn the value of m^*/m is large and is in the ferromagnetic region and this is contrary to the experimental fact that Mn is not ferromagnetic. The reason for this contradiction is not clear at present. The values of m^*/m given in the sixth column of the upper half

of Table I are derived from (9.1) by using the free electron approximation in which $\rho(\xi_0)$ is equal to $3N/(4\xi_F)$.

In the second model shown in Fig. 3(b), the low temperature electronic specific heat per positive hole is given by

$$C_e = \frac{\pi^2 k^2 T}{3N} \rho(\xi_0') = \frac{\pi^2 k^2 T}{k_0' (d\varepsilon/dk)_{k=k_0'}}, \quad (9.2)$$

where $\xi_0' = \varepsilon(k_0')$. ξ_0' is given by a formula similar to (6.15) only if k_0 , k_0' , and ξ_F are replaced by k_0' , k_0' and $\xi_F' = \hbar^2 k_0'^2/2m^*$ respectively. $(d\varepsilon/dk)_{k=k_0'}$ in (9.2) is calculated from $\varepsilon(k)$, (4.4). In this case it is enough to consider only $\varepsilon_{s,r}^p(k)$. Although r_s is not so small as one can see in the lower half of Table I, we make use of the approximation, $\varepsilon_{s,r}^p(k) \approx \varepsilon_{s,r}^a(k)$, because the integrations involved in $\varepsilon_{s,r}^p(k)$ are difficult, and then $\varepsilon_{s,r}(k) \approx \varepsilon_{s,r}^a(k)$.^{*} Using Fletcher and Larson's calculations of $(d\varepsilon_{s,r}^a/dk)_{k=k_0'^{16}}$ and k_0' given by (3.4), we obtain the values of m^*/m , from (9.2) and (6.17) and (6.20) with k_0' instead of k_0 , so as to explain the observed low temperature electronic heat. The values of m^*/m for Ni, Co and Fe are given in the seventh column of the lower half of Table I and are indicated by triangles in Fig. 1. All the triangles are below curve (1) and this means that the magnitude of the magnetization of the positive hole gas, having r_s and m^*/m at the points denoted by triangles, at 0°K is smaller than the one when all the spins of the positive holes are parallel. This contradicts with the initial assumption. As the effect of the correlation on the state density at the Fermi surface, $\rho(\xi_0')$, becomes serious in the case of the larger r_s , in order to arrive at a more satisfactory agreement, it is necessary to make a more precise approximation, that is, higher-order perturbation calculations. The values of m^*/m given in the sixth column of Table I are obtained by the free electron model, where $\rho(\xi_0') = 3N/(4\xi_F')$, and are the values tabulated in the various text books²⁸⁾.

In §7 the expressions for the Curie temperature and the paramagnetic susceptibility

above the Curie point of an electron gas has been given by (7.7) and (7.8) as functions of only r_s and m^*/m respectively. In §8 the magnitude of the magnetization at 0°K and its variation with temperature at low temperatures have been given by (8.28) or (8.33), and (8.30), (8.35) or (8.36) respectively. C_1 , C_2 , C' and C'' in these formulas are given by (6.20), (6.21), (6.24) and (6.25) respectively and are rewritten as follows:

$$C_1 = 1 + (m^*/m)D_1, \quad (9.3)$$

$$C_2 = 1 + (m^*/m)D_2, \quad (9.4)$$

$$C' = 2C_1^{-4}(1 + (m^*/m)F' + (m^*/m)^2G'), \quad (9.5)$$

$$C'' = (4/3)C_1^{-4}(1 + (m^*/m)F'' + (m^*/m)^2G''). \quad (9.6)$$

D_1 in (9.3), D_2 in (9.4), F' and G' in (9.5), and F'' and G'' in (9.6) are all functions of only r_s , and are illustrated in Fig. 4 only when the approximation that $\varepsilon_{s,r}(k) = \varepsilon_{s,r}^a(k)$ is taken. In the case of model (a) the approximation, $\varepsilon_{s,r}(k) = 2\varepsilon_{s,r}^a(k)$, and in the case of model (b) the approximation, $\varepsilon_{s,r}(k) = \varepsilon_{s,r}^a(k)$, will be taken up in the following considerations. The coefficients of the molecular fields for model (a) and for model (b) in the neighbourhood of and above the Curie temperature are given by α in (4.11). The one for model (b) at low temperature is given by α_N in (4.16). α and α_N are also functions only of

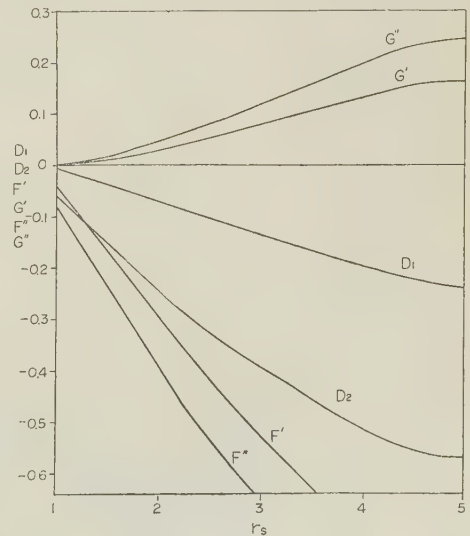


Fig. 4. Numerical results of D_1 , D_2 , F' , G' , F'' , and G'' in (9.3), (9.4), (9.5) and (9.6). Fletcher and Larson's calculation¹⁶⁾ on the one-electron energy and its derivatives are made use of.

* When r_s is large, we can introduce the approximation that $\varepsilon_{s,r}^p(k) \approx 0$, that is $\varepsilon_{s,r}(k) \approx 0$ in this case, but the values m^*/m for Ni, Co, and Fe determined from (6.17), (6.20) and (9.2) with this approximation becomes all negative. Then the approximation in the text will be more satisfactory.

r_s , as shown in Fig. 5. In all these cases, the gases are assumed to be degenerate.

Then, using the numerical results shown in Figs. 4 and 5 and the values of m^*/m given in the seventh column of Table I, we obtain the theoretical values of the Curie temperatures T_c for Ni, Co and Fe from (7.7) in the cases of models (a) and (b) in Fig. 3, and these are shown in the second column of

Table II with the observed values of $T_c^{(29)}$. The calculated values for Co in Table II correspond to the f.c.c. Co and the values for the h.c.p. Co are almost the same. As mentioned above, α , instead of α_N , is used also in the theoretical evaluations of T_c and ξ based on model (b).

The relations between $1/\chi$ and T of Ni, Co and Fe have been hitherto understood to follow the Curie-Weiss law. The variation with temperature of $1/\chi$ for Ni has been frequently observed⁽³⁰⁾⁻⁽³³⁾ and does not follow either the Curie-Weiss law or the relation given by (7.9). Only in the immediate neighbourhood of the Curie temperature, we can interpret the observed $1/\chi$ vs. T curve for Ni either by the Curie-Weiss law or by the relation (7.9), but in the higher temperature regions we cannot, and both the curves showing the variation of $1/\chi$ with T and T^2 are concave downwards, as shown in Figs. 6 and 7. In the neighbourhood of the temperature just below the melting point of Ni, the susceptibility follows the Curie-Weiss law (Fig. 6). The observed value of ξ for Ni given in Table II is tentatively calculated

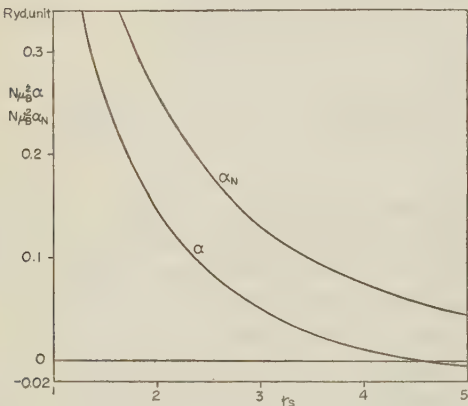


Fig 5. The coefficients of the molecular field α and α_N are given as functions of r_s when $n \ll N$ and $n \approx N$, respectively.

Table II. Curie temperatures T_c , temperature coefficients of susceptibilities above the Curie temperature, ξ , and temperature coefficients of spontaneous magnetizations at low temperatures $\delta_{3/2}$ and δ_2 , for Ni, Co and Fe.

Element	T_c °K	ξ (c.g.s.)	δ_2 (°K) ⁻²	$\delta_{3/2}$ (°K) ^{-3/2}	
Ni	Model (a)	1.28×10^4	5.87×10^4	3.05×10^{-9}	4.98×10^{-8}
	Model (b)	6.76×10^3	3.24×10^4	—	2.08×10^{-6}
	Experiment	6.31×10^3 ^a	5.52×10^3 ^b	3.58×10^{-7} ^d	$\begin{cases} 5.02 \times 10^{-6}$ ^d \\ 8.61×10^{-6} ^f \end{cases}
Co	Model (a)	1.13×10^4	1.35×10^4	3.62×10^{-9}	9.78×10^{-8}
	Model (b)	1.50×10^4	9.23×10^4	—	8.57×10^{-7}
	Experiment	1.39×10^3 ^a	3.20×10^4 ^c	4.41×10^{-8} ^e	$\begin{cases} 1.46 \times 10^{-6}$ ^e \\ 2.91×10^{-6} ^f \end{cases}
Fe	Model (a)	1.06×10^4	1.71×10^4	4.47×10^{-9}	1.06×10^{-7}
	Model (b)	1.71×10^4	8.60×10^4	—	7.31×10^{-7}
	Experiment	1.04×10^3 ^a	2.11×10^3 ^b	6.22×10^{-8} ^d	$\begin{cases} 2.81 \times 10^{-6}$ ^d \\ 3.47×10^{-6} ^f \end{cases}

a R. M. Bozorth: *Ferromagnetism* (D. Van Norstrand Company, Inc., New York, 1951) 871.

b The values are calculated from the experimental measurements of susceptibilities by E. M. Terry: Phys. Rev. **9** (1917) 394 and Y. Nakagawa: J. Phys. Soc. Japan **11** (1956) 855. (See Fig. 7 and 9.)

c The value is calculated from the experimental measurements of susceptibilities by M. Fallot: J. phys. radium **5** (1944) 153. (See Fig. 8.)

d The values are calculated from the experimental measurements of spontaneous magnetization by M. Fallot: Ann. physique **6** (1936) 305.

e The values are calculated from the experimental measurements of spontaneous magnetization by K. Honda and H. Masumoto: Sci. Repts. Tohoku Imp. Univ. **20** (1931) 323.

f The values are determined only from the $T^{3/2}$ law, (8.36).

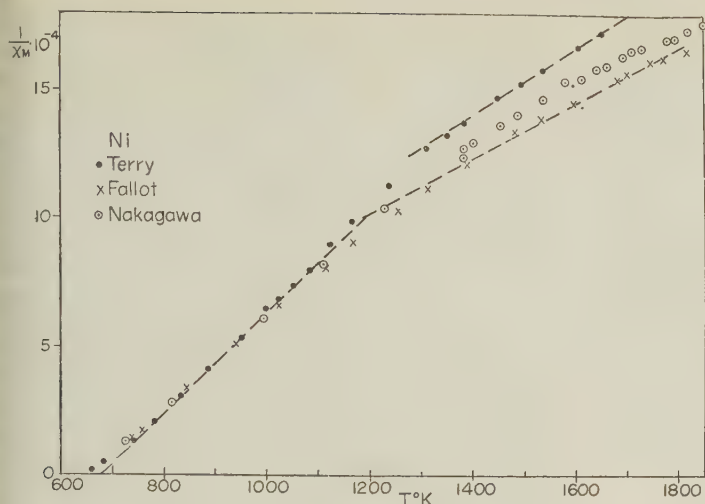


Fig. 6. The experimental results of $1/\chi$ vs T for Ni are reproduced. ● shows Terry's, × Fallot's, and ○ Nakagawa's data^{30,32,33}.

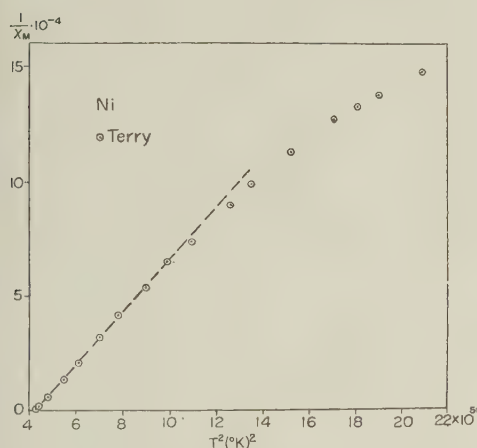


Fig. 7. Terry's datum in Fig. 6 is shown as the relation $1/\chi-T^2$ for Ni³⁰.

from (7.9) and the curve $1/\chi-T^2$ in Fig. 7 at comparatively lower temperatures. Further discussion on the χ of Ni will be postponed to § 11. The $1/\chi-T^2$ curves for Co are shown in Fig. 8^{30,32,33}, and are almost straight lines except in the neighbourhoods of the Curie point and the melting point. Especially Fallot's data³² are well in accord with the relation (7.9), and are made use of to calculate ξ for Co. There are transformations in Fe, and α and δ phases have body-centered cubic lattices with nearly equal lattice constants. Then the curves $1/\chi-T^2$ observed both in α and δ phases^{30,33} are considered as a single straight line as shown in Fig. 9 and from

this line the value of ξ for Fe is calculated. The linear relation between $1/\chi$ and T^2 in γ Fe^{30,32,33} will be analyzed in § 10.

The theoretical values of ξ for models (a) and (b) are obtained from (7.10), and the numerical values in Table I and Fig. 4, and are given in the third column of Table II, also with the observed values of ξ determined above.

The experiments on the variation with temperature of spontaneous magnetization at low temperatures are few, and we make use of the observations on Ni and Fe by Fallot³⁴ and on Co by Honda and Masumoto³⁵. The observed values of $\delta_{3/2}$ and δ_2 are determined from their results so that the observed variations of magnetizations satisfy the formula (8.30). Also the observed values of $\delta_{3/2}$ are obtained from the $T^{3/2}$ law, (8.36). The theoretical values of δ_2 only for model (a) are calculated from (8.29) and the numerical values in Table I and Fig. 4, and are listed in the fourth column of Table II. In order to find the theoretical values of $\delta_{3/2}$ in model (a), the values of m_0 given by (8.28) is necessary as shown by (8.31). The values of m_0 depend

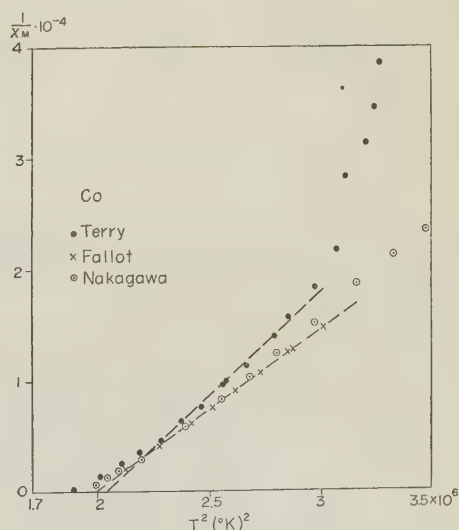


Fig. 8. The experimental results of $1/\chi$ vs T^2 for Co are shown. ● shows Terry's, × Fallot's, ○ Nakagawa's data^{30,32,33}.

very sensitively upon the values of m^*/m . Then we assume the following values of m_0 in accordance with the experimental facts: namely $m_0=0.06$ for Ni, $m_0=1.7/9=0.19$ for Co, and $m_0=2.2/8=0.275$ for Fe. (We can obtain these values for m_0 from (8.28), if m^*/m for Ni, Co, and Fe are 2.91, 2.83 and 2.77 respectively. These values of m^*/m are not so different from those in the upper half of Table I.) Once m_0 is determined, $\delta_{3/2}$ does not depend on m^*/m but only on r_s . From (8.23), (8.31) and the values of m_0 fixed above the theoretical values of $\delta_{3/2}$ in model (a), and from (8.25) the theoretical values of $\delta_{3/2}^N$ in model (b), are obtained, and are listed in the fifth column of Table II.

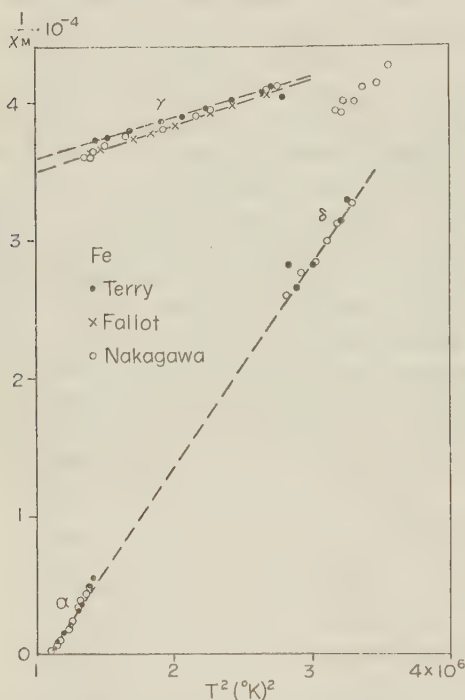


Fig. 9. The experimental results of $1/\chi$ vs T^2 for Fe are shown. ● shows Terry's, × Fallot's, and ○ Nakagawa's data^{30,32,33}.

If we compare the theoretical values with the observed values in Table II, for $\delta_{3/2}$ the results of model (b) are closer to the observed values than those of model (a). On the contrary, for ξ the results of model (a) are better. If one takes into account the fact that the approximation of the expansion in powers of $(\kappa T/\zeta_F)^2$ in (6.23) is not so satisfactory in the neighbourhood of the Curie temperature, it will be concluded that model (b) is

better in Ni, Co and Fe for the quantitative explanations of the experimental results. In particular, the values of $\delta_{3/2}$ based on model (b) agree very well with the observed values, nevertheless the approximation in § 8 for the calculation of $\delta_{3/2}$ is simple and rough. From the experiments the values of $T_0^2\delta_2$ becomes 0.142 in Ni, 0.0857 in Co, and 0.0678 in Fe respectively, and do not satisfy the relation (8.37). This disagreement may be partly due to the fact that the Weiss approximation and the method of determination of δ_2 from the experimental results are not so satisfactory, but will be mainly due to the fact that model (a) is not so satisfactory a model for the ferromagnetic transition metals, Ni, Co and Fe.

§ 10. Comparison with Experimental Results of Paramagnetic Transition Metals

The paramagnetic susceptibility of the degenerate electron gas in the non-ferromagnetic case is given by (7.13), (7.14) and (7.15). From the experimental values of $1/\chi_0$ and η we can fix the values of r_s and m^*/m for the paramagnetic transition metals. The linear relations between $1/\chi$ and T^2 given by (7.13) are fairly well realized in the experimental results on γ -Fe by Terry³⁰ and Fallot³² and on Pd and Pt by Hoare and Matthews³⁶, as shown in Figs. 9 and 10 respectively. At lower temperatures the curves $1/\chi-T^2$ of Pd and Pt becomes anomalous. The experimental values of $1/\chi_0$ and η in γ -Fe, Pd and Pt are obtained from Figs. 9 and 10 and the values of the susceptibilities of Pd and Pt at the room temperature³⁶, and are tabulated in

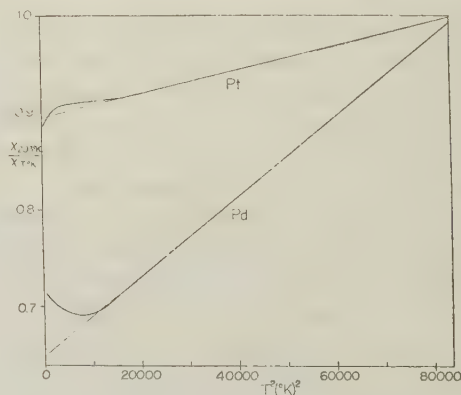


Fig. 10. The experimental results of $\chi_{293^\circ\text{K}}/\chi_{T^\circ\text{K}}$ vs T^2 for Pd and Pt by Hoare and Matthews³⁶ are shown.

Table III. Temperature dependences of paramagnetic susceptibilities of γ Fe, Pd and Pt.

Element	$1/\chi_0$ c.g.s.	γ c.g.s.
γ Fe	3.99×10^3	3.6×10^{-4}
Pd	1.04×10^4	6.5×10^{-2}
Pt	4.29×10^4	6.0×10^{-2}

Table III.

From the experimental values fixed above, the numerical results in Fig. 4 and (4.11), (6.17), (7.14), (7.15), (9.3) and (9.5), we obtain the values of r_s and m^*/m of the magnetic carriers for γ Fe, Pd and Pt, which are shown in the second and third columns of Table IV, where the approximation, $\mathcal{E}_{s,r.}(k) = \mathcal{E}_{s,r.}^0(k)$ is used in D_1 , (9.3), F' and G' , (9.5), as all the values of r_s in this case are comparatively large. The values of r_s and m^*/m for γ Fe, Pd and Pt thus determined are shown in Fig. 1 by squares. The squares for Pd and Pt lie above curve (1). This will be attributable to the difference between the approximations which are taken to obtain curves (1) and (6). From the r_s and the lattice constants the numbers of the magnetic carriers (or positive holes) per atom, p , are obtained as in the sixth column of Table IV.

Table IV. Mean distances r_s , effective masses m^*/m , crystal structures, lattice constants²⁷⁾, and effective numbers of magnetic carriers (or positive holes) per atom p , of γ Fe, Pd and Pt.

Element	r_s a.u.	m^*/m	crystal structure	lattice constant Å	number of positive holes per atom p
γ Fe	2.98	3.13	f.c.c.	3.65	0.69
Pd	4.18	3.82	f.c.c.	3.88	0.32
Pt	4.31	3.72	f.c.c.	3.92	0.30

constant C per mole, (7.2), and θ_p , (7.3), are obtained as 0.199 and $\sim 50^\circ\text{K}$, respectively. We can find the values 0.530 for the number of the positive holes per atom, p , in Pd from this Curie constant and 3.16×10^{-4} Ryd. unit for the coefficient of the molecular field, $\alpha N \mu_B^2$, from θ_p in Pd. Although α is positive, α is very small and this can be expected in the non-degenerate gas. The value of p in this case is different from the value in Table IV. This difference may be attributed to the increase of the number of the positive holes which arises from the s-d transfer of

As shown in Fig. 11, the susceptibility of Pd at higher temperature shows the Curie-Weiss law³⁷⁾⁻³⁹⁾. It will be seen in § 11 that the degeneracy temperature of Pd is about 1300°K (T_0' in Table VI). At higher temperatures than the degeneracy temperature, from the discussion at the beginning of § 7, the susceptibility of the gas is considered to follow the Curie-Weiss law, (7.1), (7.2) and (7.3). From Wucher's data^{38), 39)}, the Curie

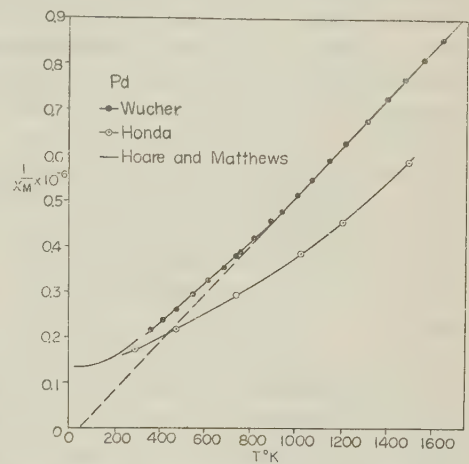


Fig. 11. The experimental results of $1/\chi$ vs T for Pd by Honda³⁷⁾, Hoare and Matthews³⁶⁾ and Wucher^{38), 39)} are shown.

electrons at higher temperatures, or may be due to the error of the expansions in C_1 , (9.3), and C' , (9.5), when r_s is determined from (7.14), (7.15) and the data in Fig. 10. The values p of Pd and Pt in Table IV are a little greater than the values derived from the Stoner theory by Hoare and Matthews³⁶⁾, but are smaller than the well-known value 0.6 which has been estimated in the following way^{40), 41)}. According to the measurements of the susceptibility on Pd-alloys with noble metals⁴²⁾, the susceptibility decreases with the increasing concentration of noble metals and

becomes zero when 60 per cent of the noble metals has been added. These results has been interpreted as showing that in pure Pd there is about 0.6 electron per atom in 5s states and the same number of vacant 4d states, and that when a noble metal is alloyed with Pd the valence electrons of the noble metal go into one of the 4d states until all the 4d levels are filled. Then p in Pd and similarly in Pt are expected to be 0.6. However, the decreases in susceptibility are not necessarily linear with the concentrations of the noble metal. The rates of the decreases in the region of low concentrations show that the value of p for Pd is about 0.3. The same will be said of the case of Pt.

Table V. Electronic specific heats of Pd and Pt.

Element	$\gamma_{\text{calc.}}$	$\gamma_{\text{exp.}}$	m^*/m
Pd	16.4	26~31	4.32
Pt	16.0	16	3.72

Using the values of r_s , m^*/m and p in Table IV, we obtain the coefficients of the electronic specific heat, γ , for Pd and Pt from (9.1), and these are shown in Table V with the experimental values. The agreement is quite satisfactory for Pt. The difference between $\gamma_{\text{calc.}}$ and $\gamma_{\text{exp.}}$ for Pd becomes smaller if we use the larger value of p so as to explain the data of susceptibility at higher temperatures. The values of m^*/m in the fourth column of Table V are determined so as to get the experimental values of γ from r_s in Table IV. These values of m^*/m are roughly equal to values determined from the susceptibility in Table IV. In the case of γFe , as the electronic specific heat in the γ phase is not known, the values of r_s , m^*/m , and p of γFe given in Table IV are not examined from a different point of view at present. Recently Marshall and Weiss have reported that in γFe approximately seven 3d electrons per atom are found by X-ray diffraction experiment²⁰⁾. From this the number of holes per atom in 3d band of γFe becomes three, and the value of p for γFe given in Table IV is fairly smaller than three. If we neglect the term of the short-range correlation in C' in (7.15), we can obtain 2.2 for p of γFe and 2.04 for r_s of γFe without changing the value of m^*/m by the same method given

above.

§ 11. Discussions and Conclusions

In § 9 and § 10 the magnetic properties of ferro- and para-magnetic electron gases have been compared with those of real ferro- and para-magnetic transition metals and an almost satisfactory agreement has been obtained. However, the variation with temperature of χ of Ni is not so simple, and Watanabe⁴³⁾ and Wohlfarth⁴⁾ have shown that if the effect of the s-d transfer of electrons is taken into account the number of the positive holes in 3d-band increases with temperature and accordingly the decrease of χ due to the thermal motion is reduced. It should be noted that as the degeneracy of the gas is lifted at higher temperatures the relation between $1/\chi$ and T will be given rather by the Curie-Weiss law than the relation (7.9) in Ni. In the Curie-Weiss law, the coefficient of the molecular field, α , may be very different from that given by (4.11). Now we shall examine the temperature, at which the degeneracy of the positive hole gas in model (b) is lifted, in the following way. From (6.16), T_0 , which satisfy $\zeta_F = \kappa T_0$, are shown in the second column of Table VI. The temperature T_0' at which the second term in the expansion (7.6) becomes comparable to the first term,

Table VI. Degeneracy temperature T_0 , T_0' and the widths of the distribution, $\Delta = \kappa T_0''$, of Ni, Co, Fe in model (b), and T_0 and T_0' of Pd and Pt.

Element	T_0 °K	T_0' °K	T_0'' °K
Ni	1.04×10^4	4.55×10^3	2.52×10^3
Co	1.87×10^4	2.58×10^3	8.52×10^3
Fe	2.11×10^4	3.78×10^3	9.94×10^3
Pd	8.72×10^3	1.32×10^3	—
Pt	8.42×10^3	1.26×10^3	—

namely, $T_0'^2 = 24\zeta_F^2/(\pi^2\kappa^2C')$, are given in the third column of Table VI. The widths of the electron distribution at 0°K, that is, the differences between the one-electron energies with $k=0$ and $k=k_0'$, Δ , are obtained from (4.4) as shown by Fletcher and Larson¹⁶⁾: $\Delta = \varepsilon(k_0') - \varepsilon(0) = \kappa T_0''$. The values of T_0'' in model (b) for Ni, Co and Fe are calculated as in the fourth column of Table VI. As seen from Table VI, T_0' in Ni is low and is not so

different from T_c . This means that the expansion (6.23) above T_c is an unsatisfactory approximation in Ni and we cannot treat the positive holes as a degenerate gas. Therefore, the numerical values of T_c and ξ for Ni based upon model (b) in Table II may be doubtful, as they are calculated from the expansion (6.23). It is desirable to calculate T_c and χ from (7.12) respectively without the procedure of expansion. There is a very difficult problem that in order to obtain the state density in the non-degenerate state we cannot use the one-electron energy $\varepsilon(\mathbf{k})$ given by (4.4) because this one-electron energy is the energy in the degenerate state. The one-electron energy in the non-degenerate state of gas will be dependent upon the distribution. At such higher temperature, however, that degeneracy is completely lifted, the electron-electron interactions and accordingly the molecular field are neglected in comparison with the thermal motion of electrons (or positive holes), and we can expect that the electron gas (or positive hole gas) follows the Curie-Weiss law or the Curie law. It seems that in Ni this circumstance occurs. We can expect the Curie-Weiss law or the Curie law to hold in any metal if the degeneracy of the electron gas in the metal is completely lifted, although we cannot observe such behavior frequently as the degeneracy temperatures of most metals are higher. It is expected from Table VI that the effect of the non-degeneracy on the susceptibilities of Pd and Pt will be above 1000°K . Actually in Pd the variation with temperature of susceptibility agrees with (7.13) at lower temperatures and nearly with the Curie law at higher temperatures (Figs. 10 and 11). The same property will be found in Pt.

In §5 we have discussed the possibilities of ferromagnetism of an electron gas, and arrived at the conclusion that the electron gas having heavier effective mass by which only the thermal kinetic energy is reduced can show ferromagnetism. In §9, we have taken models (a) and (b) to compare the magnetism of an electron gas with that of the real metallic ferromagnets and we have concluded that model (b) is better in comparison with the experimental results. It is a fundamental and important problem whether model (b) will faithfully describe the state of 3d band, that

is, whether we can separate the individual motion of electrons such as model (b) from the total Hamiltonian of electrons in crystal. Nozières and Pines⁴⁴⁾ have also shown that in most metals the eigen-motion of plasma oscillation is well defined and there exists the individual motion of electrons with the screened Coulomb interactions. And it is certain that when the excitation of the lower energy as compared with the plasma energy is considered the subsidiary condition may be ignored^{44), 45)}. The effect, however, of the correlation on the minority carriers, such as in model (b), is not yet clearly understood. It will be supposed that the long-range part of the Coulomb interaction between the minority carriers may be described by the minority carrier plasma, and the Coulomb interaction becomes the screened interaction. This minority carrier plasma will couple with the majority carrier plasma. If in the ferromagnetic transition metal the coupling is weak, and if the minority carrier plasma is well defined, and if the quantum of the plasma is not excited at ordinary temperature as the energy is high, model (b) will be a proper model to explain the magnetism of the transition metal. Even if the minority carrier plasma does not exist, the Coulomb interaction between minority carriers will be screened by any plasma oscillation existing in the metal. It is an interesting and difficult problem to show whether the screening of the Coulomb interaction between holes in the 3d band is determined by the plasma of positive hole gas itself or by the plasma of electrons in 3d and 4s bands, although the former has been assumed in this paper. It may be useful to determine k_e so as to fit the theoretical value of $\delta_{3/2}$ with its experimental value at present.

For actual metallic densities Nozières and Pines¹⁸⁾ have shown that the contribution to the correlation energy from long-wavelength momentum transfers is accurately calculated in the random phase approximation. They have calculated this contribution using the B-P collective description. Moreover, if all remaining interaction terms in the B-P description are calculated by the perturbation theory and these results show convergence at actual metallic densities, the B-P description will be justified at these densities, and the tendency

of the convergence in the perturbation calculations has already been shown^{18), 46)}. Then there will be no doubt as to the validity of the B-P method in studying the magnetism of an electron gas at actual metallic densities. In the meantime, it is worth notice that when m^*/m is large or r_s is large, the electron gas becomes unstable and a certain lattice structure of electrons becomes stable⁴⁶⁾. In the case where the electron gas has the values of r_s and m^*/m from which C_1 given by (6.20) or (9.3) becomes negative, we find that (from (6.17) the state density on the Fermi surface has a negative value, or) from (6.3) $(d\varepsilon/dk)_{k=k_0} < 0$. This fact means that the electron gas is unstable in energy and there is another stable configuration of electrons such as an electron lattice. The relation between r_s and m^*/m which satisfies $C_1=0$ is shown by curve (8) in Fig. 1⁴⁷⁾. In the upper region of curve (8), the model of the electron gas is meaningless.

It may be given as a conclusion that the model of the electron gas to explain the magnetism of the transition metals is not a well-established model, but is almost consistent with the various experimental results qualitatively and semi-quantitatively. We have taken only the case of pure metals. It will be a proper judgment to the model of the electron gas whether we can explain the magnetism of alloys too. Although we have determined the values of m^*/m so as to be consistent with observed electronic specific heats, it is desirable to calculate the effective mass theoretically as in the alkali metals, etc. From Fletcher's calculations on the 3d-band structure of Ni⁴⁸⁾, the effective mass is estimated as $m^*/m \sim 40$ and is larger than that given in Table I. By using the effective mass we have partly taken into account the periodic lattice potential, and if the effect of the lattice potential on the wave function of electrons is taken into consideration, the experimental fact of the neutron diffraction that a certain number of spins per atom is bound on each atom will be explained.

The coefficient $\delta_{3/2}$ of the variation with temperature of spontaneous magnetization, as shown in §8, is related directly to the electron-electron interactions, the observed values of $\delta_{3/2}$ are useful and the experiments on the variation of magnetization at low tem-

peratures are desirable. As the approximation taken in the calculation of the eigen-energy of the spin-wave motion in §8 seems to be rough, it will be necessary to proceed by better approximation.

The linear relation between $1/\chi$ and T^2 which experimentally holds in γ Fe, Pd and Pt has been satisfactorily explained from the collective model of the electron gas in §10, the agreements with the experiments on the electronic specific heat are satisfactory, and it is doubtful only from the relation between $1/\chi$ and T at higher temperatures that these metals are antiferromagnetic.

In conclusion the author wishes to express his sincere thanks to Prof. R. Kubo for consultations and criticism of the manuscript and valuable discussion.

Appendix. The Correction of Non-Orthogonality to the Exchange Integral

In §8 we have employed the localized wave functions (8.1) and (8.4). They have been non-orthogonal with one another, and we consider the correction of this non-orthogonality. As shown by Van Vleck²¹⁾, when the orbital wave functions are non-orthogonal with one another, the effective exchange integral between the orbits localized at $\mathbf{R}$ and $\mathbf{R}'$, in the vector model, is given for the first approximation by

$$J_{\mathbf{RR}'}^{\text{eff}} = V_{\mathbf{RR}'} - \Delta_{\mathbf{RR}'} V^0, \quad (\text{A1})$$

where $V^0 = \int \cdots \int \Psi^* \mathcal{H} \Psi dv_1 \cdots dv_n$, $V_{\mathbf{RR}'} = \int \cdots \int \Psi^* \mathcal{H} P_{\mathbf{RR}'} \Psi dv_1 \cdots dv_n$, and $\Delta_{\mathbf{RR}'} = \int \cdots \int (P_{\mathbf{RR}'} \Psi^*) \Psi dv_1 \cdots dv_n$, and $\mathcal{H}$ is the total Hamiltonian of n electrons, and is written as the sum of one-electron Hamiltonians and interactions: $\mathcal{H} = \sum_i H_i + \sum_{i>j} v_{ij}$, Ψ is the product of the n localized wave functions given by (8.1) or (8.4), and $P_{\mathbf{RR}'}$ is a permutation operator on $\mathbf{R}$ and $\mathbf{R}'$. Then $J_{\mathbf{RR}'}^{\text{eff}}$ becomes

$$\begin{aligned} J_{\mathbf{RR}'}^{\text{eff}} = & J_{\mathbf{RR}'} + S_{\mathbf{RR}'} \int \phi_{\mathbf{R}}^*(i) H_i \phi_{\mathbf{R}'}(i) dv_i \\ & + S_{\mathbf{RR}'} \int \phi_{\mathbf{R}}^*(j) H_j \phi_{\mathbf{R}}(j) dv_j \\ & - \Delta_{\mathbf{RR}'} (\varepsilon_{\mathbf{R}} - \varepsilon_{\mathbf{R}'} + I_{\mathbf{RR}'}), \end{aligned} \quad (\text{A2})$$

where $J_{\mathbf{RR}'}$ is the ordinary exchange integral given by (8.6), $S_{\mathbf{RR}'}$ is an overlap integral: $S_{\mathbf{RR}'} = \int \phi_{\mathbf{R}}^*(1) \phi_{\mathbf{R}'}(1) dv_1$, $\Delta_{\mathbf{RR}'} = |S_{\mathbf{RR}'}|^2$, $\varepsilon_{\mathbf{R}} = \int \phi_{\mathbf{R}}^*(1)$

$\cdot H_1 \phi_{\mathbf{R}}(1) dv_1$, and $I_{\mathbf{RR}'}$ is an ordinary Coulomb integral: $I_{\mathbf{RR}'} = \iint \phi_{\mathbf{R}'}^*(1) \phi_{\mathbf{R}'}^*(2) v_{12} \phi_{\mathbf{R}}(1) \phi_{\mathbf{R}}(2) \cdot dv_1 dv_2$. Using (8.1) or (8.4) for the wave function ϕ , we have, $S_{\mathbf{RR}'} = n^{-1} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')}$, $\Delta_{\mathbf{RR}'} = n^{-2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} e^{i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{R} - \mathbf{R}')}$, $\epsilon_{\mathbf{R}} = \epsilon_{\mathbf{R}'} = n^{-1} \cdot (\hbar^2/2m) \sum_{\mathbf{k}} k^2$, and $I_{\mathbf{RR}'} = \sum_{\mathbf{k}} v(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} = v(\mathbf{R} - \mathbf{R}')$, where the sums are taken only over the states occupied singly by electrons, and in $\epsilon_{\mathbf{R}}$ the constant term due to the uniform positive charge distribution is ignored because it is unimportant. Then,

$$J_{\mathbf{RR}'}^{\text{eff}} = J_{\mathbf{RR}'} - \Delta_{\mathbf{RR}'} I_{\mathbf{RR}'} + \frac{\hbar^2}{2m^* n^2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} (k^2 + k'^2) \cdot e^{i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{R} - \mathbf{R}')} - 2\Delta_{\mathbf{RR}'} \epsilon_{\mathbf{R}}. \quad (\text{A3})$$

The energy of the spin-wave with wave vector $\mathbf{K}_\lambda$ is rewritten, instead of (8.11), as

$$A_\lambda^{\text{eff}} = \sum_{\mathbf{h}} J_{\mathbf{Rh}}^{\text{eff}} (1 - \exp(i\mathbf{K}_\lambda \cdot \mathbf{R}_h)) = A_\lambda + \Delta A_\lambda' + \Delta A_\lambda'', \quad (\text{A4})$$

where A_λ is given by (8.12), and $\Delta A_\lambda'$ and $\Delta A_\lambda''$ are given by

$$\Delta A_\lambda' = \frac{1}{n} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \{v(\mathbf{k} - \mathbf{k}') - v(\mathbf{k} - \mathbf{k}' + \mathbf{K}_\lambda)\}, \quad (\text{A5})$$

$$\Delta A_\lambda'' = -\frac{\hbar^2}{2m^* n} \sum_{\mathbf{k}} \{(k + K_\lambda)^2 - k^2\} = -\hbar^2 K_\lambda^2 / 2m^*. \quad (\text{A6})$$

In the sums over $\mathbf{k}$ and $\mathbf{k}'$ in (A5), the restrictions as in the case of (8.12) are not imposed. Considering that $v(\mathbf{k})$ is a function of the absolute value of $\mathbf{k}$, $|\mathbf{K}_\lambda| \ll 1$, and the regions of $\mathbf{k}$ and $\mathbf{k}'$ over which we sum are isotropic, approximately we have,

$$\Delta A_\lambda' = (K_\lambda^2/6n) \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \{(\partial^2 v(\mathbf{k} - \mathbf{k}')/\partial|\mathbf{k} - \mathbf{k}'|^2) + (2/|\mathbf{k} - \mathbf{k}'|)(\partial v(\mathbf{k} - \mathbf{k}')/\partial|\mathbf{k} - \mathbf{k}'|)\}. \quad (\text{A7})$$

We take only the screened Coulomb interaction, (3.1), for $v(\mathbf{k})$. As the calculation of the contribution from short-range correlation is difficult, we ignore entirely the effect of short-range correlation on $\Delta A_\lambda'$. Then from (3.5) $\Delta A_\lambda'$ becomes $\Delta A_\lambda' = (4\pi e^2 K_\lambda^2/3Vn) \sum_{\mathbf{k}} \sum_{\mathbf{k}'} (k - k')^{-4}$ for $|\mathbf{k} - \mathbf{k}'| > k_e$. When $n \ll N$ as in Fig. 3(a), it is shown that $\Delta A_\lambda'$ and $\Delta A_\lambda''$ are smaller by the order n/N in comparison with A_λ and are negligible. When $n \approx N$ as in Fig. 3(b), we have

$$\Delta A_\lambda' = (2^{2/3}/4\pi) e^2 K_\lambda^2 k_0^{-1} \{ (4 \cdot 2^{1/3}/3\beta) - \frac{1}{2} - (4/3) \log 2 - (\beta^2/24 \cdot 2^{2/3}) + \log \beta \}. \quad (\text{A8})$$

From (8.17), (8.18), (A4), (A6) and (A8), we can obtain A_λ^{eff} in the case where $n \approx N$. From the A_λ^{eff} determined in this way and the numerical values in Table I, the numerical values of δ_N or $\delta_{N/2}^N$ given by (8.25) are found to be $2.16 \times 10^{-6} (^{\circ}\text{K})^{-3/2}$ for Ni, $6.06 \times 10^{-7} (^{\circ}\text{K})^{-3/2}$ for Co (f.c.c.) and $5.07 \times 10^{-7} (^{\circ}\text{K})^{-3/2}$ for Fe. These values do not differ so much from the values given in the fifth column of Table II which have been calculated without the correction of non-orthogonality.

References

- 1) F. Bloch: Z. Phys. **57** (1929) 545.
- 2) W. Heisenberg: Z. Phys. **49** (1928) 619.
- 3) E. C. Stoner: Proc. Roy. Soc. A, **154** (1936) 656; A, **165** (1938) 372; A, **169** (1939) 339.
- 4) E. P. Wohlfarth: Proc. Roy. Soc. A, **195** (1949) 434; Rev. Mod. Phys. **25** (1953) 211.
- 5) A. B. Lidiard: Proc. Phys. Soc. London A, **64** (1951) 814; A, **65** (1952) 885.
- 6) J. C. Slater: Phys. Rev. **49** (1936) 537, 931.
- 7) F. Bloch: Z. Phys. **61** (1930) 206. T. Holstein and H. Primakoff: Phys. Rev. **58** (1940) 1908. F. J. Dyson: Phys. Rev. **102** (1956) 1217, 1230. J. Van Kranendonk and J. H. Van Vleck: Rev. Mod. Phys. **30** (1958) 1.
- 8) J. C. Slater: Phys. Rev. **52** (1937) 198.
- 9) C. Herring and C. Kittel: Phys. Rev. **81** (1951) 869.
- 10) C. Herring: Phys. Rev. **85** (1952) 1003; **87** (1952) 60.
- 11) D. Bohm and D. Pines: Phys. Rev. **82** (1951) 625; **85** (1952) 338; **92** (1953) 609.
- 12) D. Pines: Phys. Rev. **92** (1953) 626.
- 13) D. Pines: *Solid State Physics* vol. **1** (Academic Press Inc., New York, 1955) 367.
- 14) R. A. Ferrell: Phys. Rev. **107** (1957) 450.
- 15) K. Sawada, K. A. Brueckner, N. Fukuda and R. Brout: Phys. Rev. **108** (1957) 507.
- 16) J. G. Fletcher and D. C. Larson: Phys. Rev. **111** (1958) 455.
- 17) M. Gell-Mann and K. A. Brueckner: Phys. Rev. **106** (1957) 364.
- 18) P. Nozières and D. Pines: Phys. Rev. **111** (1958) 442.
- 19) Details will be shown in another paper.
- 20) K. A. Brueckner and K. Sawada: Phys. Rev. **112** (1958) 328.
- 21) J. H. Van Vleck: Phys. Rev. **49** (1936) 232.
- 22) J. H. Van Vleck: Rev. Mod. Phys. **25** (1953) 220.

- 23) C. G. Shull, E. O. Wollan and W. C. Koehler: Phys. Rev. **84** (1951) 912. C. G. Shull and M. K. Wilkinson: Phys. Rev. **97** (1955) 304. C. G. Shull and E. O. Wollan: *Solid State Physics* vol. **2** (Academic Press Inc., New York, 1956) 138.
- 24) R. J. Weiss and J. J. De Marco: Rev. Mod. Phys. **30** (1958) 59; Phys. Rev. Letters **2** (1959) 148.
- 25) W. Hume-Rothery, P. J. Brown, J. B. Forsyth and W. H. Taylor: Phil. Mag. **3** (1958) 1466. B. W. Batterman: Phys. Rev. Letters **2** (1959) 47; Phys. Rev. **115** (1959) 81.
- 26) N. F. Mott and K. W. Stevens: Phil. Mag. **2** (1957) 1364. W. Lomer and W. Marshall: Phil. Mag. **3** (1958) 185. W. Marshall and R. J. Weiss: Suppl. J. Appl. Phys. **30** (1959) 220S.
- 27) R. W. G. Wyckoff: *Crystal Structures* (Intersci. Publ., Inc., New York, 1948).
- 28) e. g. C. Kittel: *Introduction to Solid State Physics*, 2nd ed. (John Wiley and Sons. Inc., New York, 1956) 259.
- 29) R. M. Bozorth: *Ferromagnetism* (D. Van Nostrand Co., New York, 1951) 871.
- 30) E. M. Terry: Phys. Rev. **9** (1917) 394.
- 31) W. Sucksmith and R. R. Pearce: Proc. Roy. Soc. A **167** (1938) 189.
- 32) M. Fallot: J. phys. radium **5** (1944) 153.
- 33) Y. Nakagawa: J. Phys. Soc. Japan **11** (1956) 855.
- 34) M. Fallot: Ann. physique **6** (1936) 305. E. Kondorsky and L. N. Fedotov: Izvest. Akad. Nauk SSSR, Ser. Fiz. **14** (1952) 432. S. Foner and E. D. Thompson: Suppl. J. Appl. Phys. **30** (1959) 229S.
- 35) K. Honda and H. Masumoto: Sci. Repts. Tohoku Imp. Univ. **20** (1931) 323. H. P. Myers and W. Sucksmith: Proc. Roy. Soc. A, **207** (1951) 427.
- 36) F. E. Hoare and J. C. Matthews: Proc. Roy. Soc. A, **212** (1952) 137.
- 37) K. Honda: Ann. Physik **32** (1910) 1027.
- 38) M. J. Wucher: Ann. physique. **7** (1952) 317.
- 39) M. J. Wucher: Compt. rend. **242** (1956) 1143.
- 40) E. P. Wohlfarth: Proc. Leeds Phil. Soc. **5** (1949) 89.
- 41) A. H. Wilson: *The Theory of Metals*, 2nd ed. (Cambridge Univ. Press, London, 1953) 158.
- 42) E. Vogt: Ann. Physik **14** (1932) 1. F. E. Hoare, J. C. Matthews and J. C. Walling: Proc. Roy. Soc. A, **216** (1953) 502.
- 43) H. Watanabe: J. Phys. Soc. Japan **3** (1948) 317.
- 44) P. Nozières and D. Pines: Phys. Rev. **109** (1958) 741, 762, 1062.
- 45) D. Bohm, K. Huang and D. Pines: Phys. Rev. **107** (1957) 71.
- 46) E. P. Wigner: Trans. Faraday Soc. **34** (1938) 678. J. S. Plaskett: Phil. Mag. **45** (1954) 1255. C. B. Clark: Phys. Rev. **109** (1958) 1133.
- 47) M. Shimizu: J. Phys. Soc. Japan **15** (1960) 217.
- 48) G. C. Fletcher: Proc. Phys. Soc. London A, **65** (1952) 191.

Configurational Changes of Polypeptide Molecules in the Helix-Coil Transition Region, I.*

By Kazuo NAGAI

*The Osaka Industrial Research Institute,
Daini-Nishi-2-Chome, Oyodoku, Osaka*

(Received September 29, 1959)

Formal expressions are derived for the mean square of the end-to-end distance and the electric moment of polypeptide molecules in the helix-coil transition region. It is assumed that each amino acid residue of a polypeptide molecule in the transition region is involved either in a helical section or in a randomly coiled section. A partition function of a polypeptide molecule is constructed by means of the matrix method. First, the partition function is used in obtaining the average of some scalar quantities, e.g., the mean fraction of residues involved in helical sections. Next, we obtain the average of a product of martices, which is used in calculating the mean square of the end-to-end distance and the electric moment. Expressions for the α -helix are also derived. An improved partition function including various effects, e.g., the end effect, is given in the appendix.

§ 1. Introduction

The helix-coil transition of an individual polypeptide molecule, first discovered by Doty, Yang, Blout, and their collaborators,¹⁾⁻³⁾ is very interesting and important because it bears the close relationship to the denaturation of proteins, deoxyribonucleic acid (DNA), etc. During the last few years there have been several attempts⁴⁾⁻⁹⁾ to treat this transition, which is essentially of a one-dimensional character, by statistical mechanical methods. In one⁷⁾ of these theories a good agreement with experimental data was obtained for the change in the optical rotation in the transition region. However, no attempt has been made to account for the change in mean dimensions, electric moments, and intrinsic viscosities in the transition region, which are exceedingly remarkable and of great importance as well. It is the aim of this and succeeding articles to calculate these quantities by the use of a suitable model without missing the essential character of the change in the local configuration of a polypeptide molecule in the transition region.

The calculation of these quantities seems to be significant by two reasons mentioned below. In the first place we may obtain more

detailed information on the transition by comparing the results of the present theory with experimental data. Optical rotations may be considered to depend only on the mean fraction of residues involved in helical sections and to be insensitive to the detailed distribution of helical sections along a molecular chain. Therefore, it is expected that the change in optical rotations occurs sharply at the transition region but the basic mechanism itself is rather simple. On the other hand, mean dimensions and intrinsic viscosities depend not only on the mean fraction of residues involved in helical sections but also on the distribution of helical sections along a molecular chain and the average configurations of residues involved in both helical sections and randomly coiled sections. Therefore, the change of these quantities in the transition region is more complicated, reflecting a particular circumstance of a given system. Hence, the theoretical investigation of these changes will give us more detailed information. For example, it was found that the intrinsic viscosity of poly-L-glutamic acid in 0.2 M NaCl-dioxane (2:1) solution passed through a sharp minimum preceding the normal increase with decreasing pH³⁾. The appearance of this minimum is obviously due to the fact that the molecule has the minimum mean dimension or, more precisely speaking, the minimum

* Preliminary results of this work were already published in *Busseiron Kenkyu* **2-5** (1959) 677. (in Japanese).

radius of the equivalent hydrodynamic sphere at the point, although it is not clear in what manner the change of the local configuration of the molecule takes part in this decrease in the intrinsic viscosity. Further, the change in mean dimensions and intrinsic viscosities is expected to be much more sensitive to the outset of the disruption of the α -helix than the change of the optical rotation is^{(2), (8)}.

Secondly, on the basis of the quantitative expressions derived for mean dimensions of polypeptide molecules in the transition region, we may attack, although there are many difficulties to be overcome, the problem of the biological phenomena which accompany the dimensional change in microscopic and macroscopic scales, i.e., the denaturation of proteins (e.g., the contraction of collagen on heating⁽¹⁰⁾), the contraction of muscle, the disruption of the double-stranded helix of DNA molecule on heating,⁽¹¹⁾ etc.

Expressions for mean dimensions and electric moments are obtained by constructing the partition function of a polypeptide molecule and then averaging over this partition function the square of the end-to-end distance and the electric moment, which can be expressed as sums of products of matrices of three degrees. Relations of the partition function in the present theory to those of other authors will be discussed in the next section.

Forthcoming articles of this series will involve the discussion of numerical results of the expressions obtained in this article and some theoretical study on mechano-chemical properties of individual chains and dilute gels of polypeptides in the transition region.

§2. Partition Function

For the present purpose we must choose a variable, which describes the state of each

amino acid residue ($-\text{CO}-\text{CHR}-\text{NH}-$), in such a manner that it allows us to determine the configuration of each residue uniquely if the residue is involved in a helical section and on an average if it is involved in a randomly coiled section. In this sense, it is not suitable for the present case to choose a parameter representing only whether or not the peptide nitrogen atom of each residue is hydrogen bonded as a variable.

We number all residues of a polypeptide molecule from the end with a free carboxyl group as 1, 2, $\dots$, N . Now we denote the state of the i th residue by the symbol μ_i , which is assumed to be 1 if the residue is *distorted* so as to form a helical section, and zero if it is *undistorted* or involved in a randomly coiled section. More precisely speaking, the term "*distorted*" means that the rotational angles around the three consecutive bonds, N-C, C-C and C-N of a residue have the same values as in the α -helix. This choice is similar to that of Miyake⁽⁹⁾. We assume that the peptide nitrogen atom of the i th residue is hydrogen bonded to the peptide oxygen atom of the $(i+4)$ th residue if and only if all the three residues put between them are *distorted* (See Fig. 1). The above assumption involves automatically an additional one that the rotational angle around the peptide C-N bond between the $(i+3)$ th and $(i+4)$ th residues is fixed at a certain value so as to determine the relative spatial position of the NH group and the CO group, between which the hydrogen bond is to be formed. This assumption, however, may be allowed on account of the planarity of the peptide linkage. Thus an arrangement of the digits, 0 and 1, corresponds to a state of a polypeptide molecule. Here we disregard two kinds of sequences, 010 and 0110, since these

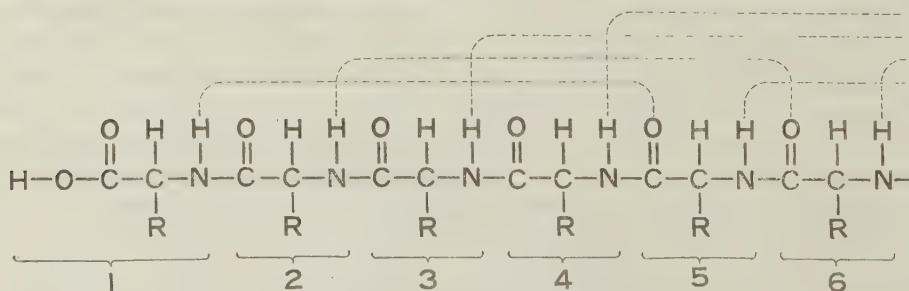


Fig. 1. Diagrammatic illustration of hydrogen bonds in the α -helix configuration of a polypeptide molecule.

states are, though not impossible, physically unreasonable. Namely, the distortion of only one or only two consecutive residues does not cause any hydrogen bond and, hence, there is no reason for these residues to be *distorted* without any decrease in free energy, which should offset the entropy decrease due to the loss of freedom. In the present model we have also neglected the possibility of the breaking of only one or only two consecutive hydrogen bonds, which does not disrupt the α -helix. However, Gibbs and DiMarzio⁷⁾ fortunately proved that this effect does not bring any significant difference into results. This seems to be due to the physical circumstance that the helix-coil transition does not occur when a hydrogen bond breaks without any other decrease in free energy, but occurs when the increase in energy on the breaking of one hydrogen bond is just balanced with some other decrease in free energy, e.g., the increase in entropy due to the increase of freedom. After all, if the former were the case, the helix $\rightarrow$ coil transition should be achieved already.

We denote the free energy of an *undistorted* residue by F_0 (per mole), that of a *distorted* residue by F_1 , and that of a hydrogen bond by F_h . Here we assume that these quantities contain the contributions not only from the polypeptide molecule under consideration but also from solvent molecules which interact with the polypeptide molecule. There is little need to discuss the interaction with solvents here, since it has already been given by Gibbs and DiMarzio⁷⁾. It is, however, quite reasonable to consider that the F_0 of a given *undistorted* residue may take two different values according to whether both of its adjacent residues are *undistorted* or, either one or both of them are *distorted*, because of the difference in steric hindrances and in the interaction with solvent molecules. Similarly, the F_1 of a given *distorted* residue may take different values according to whether it is located at the middle part of a long helical section, or very near the end, or in a rather short helical section, mainly because of the difference in freedom of side groups and the interaction of them with solvent molecules. Nevertheless, we neglect here these differences for the sake of simplicity; a general formulation of an improved partition function in-

cluding the effects mentioned above will be given in the appendix.

From F_0 , F_1 and F_h we define

$$\left. \begin{aligned} \alpha &= \exp [-(F_1 - F_0)/RT], \\ \beta &= \exp [-F_h/RT]. \end{aligned} \right\} \quad (1)$$

The physical meanings of α and β are self-evident. When the degree of polymerization, N , is sufficiently large, we may disregard the end effect with negligible error. Then, if we combine for benefit of treatment both ends to form a ring, as often done in the statistical treatment of a cooperative system, we can express the partition function in the form¹²⁾

$$Z = \sum \cdots \sum \prod_{i=1}^N \alpha^{\mu_i} \beta^{\mu_{i-1} \mu_i \mu_{i+1}}, \quad (2)$$

where $\mu_0 = \mu_N$ and $\mu_{N+1} = \mu_1$, and the summation is taken over two possible values of μ_i 's, excluding the two kinds of sequence, 010 and 0110, or

$$Z = \text{Trace} [p^N], \quad (3)$$

where p is given by

$$p = \begin{pmatrix} \alpha\beta & 0 & 0 & 0 & \alpha & 0 & 0 \\ 0 & 0 & \alpha & 0 & 0 & 0 & 0 \\ \alpha\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix}. \quad (4)$$

The matrix p has been constructed as follows. Seven possible sequences of $\mu_{i-1}, \mu_i, \mu_{i+1}$ are arranged in the order of 111, 101, 011, 001, 110, 100 and 000. Then the (k, l) -element of p , except for the $(3, 5)$ -element, is defined as $\alpha^{\mu_i} \beta^{\mu_{i-1} \mu_i \mu_{i+1}}$ with the same $\mu_{i-1}, \mu_i, \mu_{i+1}$ as the l th sequence if the second and third digits of the k th sequence are equal to the first and second digits of the l th sequence respectively, and zero otherwise. The $(3, 5)$ -element which produces the sequence 0110 is taken as zero.

The eigenvalue equation of this matrix is found to be

$$\lambda^2(\lambda - 1)(\lambda - \alpha\beta) = \alpha^3\beta. \quad (5)$$

It should be noted that this equation is equivalent to the corresponding equation given by Zimm and Bragg⁶⁾, $\lambda(\lambda - 1)(\lambda - s) = \sigma s$, if we put $\sigma = \alpha^2$ and $s = \alpha\beta$, except that the first factor in the left-hand side of Eq. (5), λ^2 , is replaced by λ in their equation. However, this difference probably introduces no signi-

ficant change into results. Further, Eq. (5) is, as can be anticipated, also equivalent to Eq. (16) in the article of Gibbs and DiMarzio⁷⁾ if we put $u=\alpha\beta/\lambda$, $x=1/\alpha\beta$ and $Z=1/\alpha$, and make n infinite. Thus, so far as only the partition function is concerned, the present theory is not new.

Now, if we express the roots of Eq. (5) by λ , λ_2 , λ_3 and λ_4 , where $\lambda > \lambda_2 \geq \lambda_3 \geq \lambda_4$, we find

$$Z = \lambda^N + \lambda_2^N + \lambda_3^N + \lambda_4^N, \quad (6)$$

which, in the limit of $N \rightarrow \infty$, becomes

$$Z = \lambda^N. \quad (7)$$

§ 3. Averages of Various Quantities

This section is concerned with the calculation of averages of various quantities determined by the state of residues. First we

calculate the average of a scalar quantity

$$f(\mu_{i-1}, \mu_i, \dots, \mu_{j+1}) = \prod_{k=i}^j f_k(\mu_{k-1}, \mu_k, \mu_{k+1}), \quad (8)$$

where $f_k(\mu_{k-1}, \mu_k, \mu_{k+1})$, ($k=i, \dots, j$), is a function determined by the state of the $(k-1)$ th, k th, and $(k+1)$ th residues. Noting that each element of the matrix $\mathbf{p}$ represents the relative probability of a given residue being in a certain specified state, we find

$$\langle f(\mu_{i-1}, \mu_i, \dots, \mu_{j+1}) \rangle = \text{Trace} [\mathbf{p}_* \mathbf{f}_i \mathbf{f}_{i+1} \dots \mathbf{f}_j], \quad (9)$$

where

$$\mathbf{p}_* = \lim_{M \rightarrow \infty} (\mathbf{p}/\lambda)^M, \quad (10)$$

and

$$\mathbf{f}_k = (1/\lambda) \begin{pmatrix} \alpha\beta f_k(1, 1, 1) & 0 & 0 & 0 & \alpha f_k(1, 1, 0) & 0 & 0 \\ 0 & 0 & \alpha f_k(0, 1, 1) & 0 & 0 & 0 & 0 \\ \alpha\beta f_k(1, 1, 1) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha f_k(0, 1, 1) & 0 & 0 & 0 & 0 \\ 0 & f_k(1, 0, 1) & 0 & 0 & 0 & f_k(1, 0, 0) & 0 \\ 0 & 0 & 0 & f_k(0, 0, 1) & 0 & 0 & f_k(0, 0, 0) \\ 0 & 0 & 0 & f_k(0, 0, 1) & 0 & 0 & f_k(0, 0, 0) \end{pmatrix}, \quad (k=i, i+1, \dots, j). \quad (11)$$

The matrix $\mathbf{p}_*$ can be obtained as follows. If $\mathbf{p}$ is diagonalized by an appropriate matrix $\mathbf{g}$ in the form

$$\mathbf{p} = \mathbf{g}^{-1} \begin{pmatrix} \lambda & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \end{pmatrix} \mathbf{g} \quad (12)$$

then, obviously $\mathbf{p}_*$ is given by

$$\mathbf{p}_* = \mathbf{g}^{-1} \begin{pmatrix} 1 & & 0 \\ & 0 & \\ 0 & & \ddots \end{pmatrix} \mathbf{g} \quad (13)$$

From Eq. (13), $\mathbf{p}_*$ is found to have the form

$$\mathbf{p}_* = \mathbf{u}\mathbf{v}, \quad (14)$$

where $\mathbf{u}$ and $\mathbf{v}$ are a row vector and a column vector, respectively,

$$\mathbf{u} = (u_1 \ u_2 \ \dots \ u_7)^T, \quad \mathbf{v} = (v_1 \ v_2 \ \dots \ v_7). \quad (15)$$

From Eqs. (12), (13) and (14), it is found that $\mathbf{u}$ and $\mathbf{v}$ are the right-hand side and the left-hand side eigenvectors of $\mathbf{p}$, associated with λ , respectively, i.e.,

$$\begin{cases} (\mathbf{p} - \lambda \mathbf{E})\mathbf{u} = \mathbf{0}, \\ \mathbf{v}(\mathbf{p} - \lambda \mathbf{E}) = \mathbf{0}, \end{cases} \quad (16)$$

$\mathbf{E}$ being the unit matrix. Solving Eq. (16), we have

$$\begin{cases} u_2 = u_4 = (\alpha^2\beta/\lambda^2)u_1, \\ u_3 = (\alpha\beta/\lambda)u_1, \\ u_5 = u_6 = u_7 = \{(\lambda - \alpha\beta)/\alpha\}u_1, \end{cases} \quad (17)$$

and

$$\begin{cases} v_2 = v_6 = (\alpha/\lambda^2)v_1, \\ v_3 = \{(\lambda - \alpha\beta)/\alpha\beta\}v_1, \\ v_4 = v_7 = \{(\lambda - \alpha\beta)/\alpha^2\beta\}v_1, \\ v_5 = (\alpha/\lambda)v_1. \end{cases} \quad (18)$$

From the relation, $\mathbf{p}_*^2 = \mathbf{p}_*$, we find the factor, u_1v_1 , which is left undetermined in Eq. (14), to be

$$c = u_1v_1 = \frac{\lambda(\lambda-1)}{4\lambda^2 - 3(1+\alpha\beta)\lambda + 2\alpha\beta}. \quad (19)$$

First, the average of the fraction of residues involved in helical sections, ξ , is equal to that of a function

$$f(\mu_{i-1}, \mu_i, \mu_{i+1}) = \begin{cases} 1 & \text{if } \mu_i = 1, \\ 0 & \text{otherwise.} \end{cases} \quad (20)$$

Introducing Eq. (20) into Eq. (9), we get

$$\xi = \frac{(\lambda-1)(3\lambda-2\alpha\beta)}{4\lambda^2-3(1+\alpha\beta)\lambda+2\alpha\beta}, \quad (21)$$

which, of course, is also obtainable from the relation, $\xi = \partial \ln \lambda / \partial \ln \alpha$.

Next, we calculate the probability, η , of the specified two consecutive residues being in the state, 10. Obviously, η , multiplied by N , denotes the average frequency of the alternation of helical sections to randomly coiled sections on the molecular chain. Similarly, we find

$$\eta = \frac{\alpha^3\beta}{\lambda^2\{4\lambda^2-3(1+\alpha\beta)\lambda+2\alpha\beta\}}. \quad (22)$$

Then the average numbers of residues involved in a helical section and in a randomly coiled section are given by

$$m_1 = \xi/\eta = (3\lambda-2\alpha\beta)/(\lambda-\alpha\beta), \quad (23)$$

and

$$m_0 = (1-\xi)/\eta = \lambda/(\lambda-1), \quad (24)$$

respectively.

Last, we calculate the average of a product of matrices

$$F(\mu_i, \mu_{i+1}, \dots, \mu_j) = F_i(\mu_i)F_{i+1}(\mu_{i+1}) \cdots F_j(\mu_j), \quad (25)$$

where $F_k(\mu_k)$, ($k=i, \dots, j$), is any matrix determined by the state of the k th residue. By using a method similar to that described above, we obtain

$$\langle F(\mu_i, \mu_{i+1}, \dots, \mu_j) \rangle = \text{Trace} [Q_* F_i F_{i+1} \cdots F_j], \quad (26)$$

where

$$Q_* = \begin{pmatrix} u_1 v_1 E & u_1 v_2 E & \cdots & u_1 v_7 E \\ u_2 v_1 E & u_2 v_2 E & \cdots & u_2 v_7 E \\ \vdots & \vdots & \ddots & \vdots \\ u_7 v_1 E & u_7 v_2 E & \cdots & u_7 v_7 E \end{pmatrix}, \quad (27)$$

E being the unit matrix of the same degrees as $F(\mu_i, \dots, \mu_j)$,

$$F_k = (1/\lambda) \begin{pmatrix} \alpha\beta F_k(1) & 0 & 0 & 0 & \alpha F_k(1) & 0 & 0 \\ 0 & 0 & \alpha F_k(1) & 0 & 0 & 0 & 0 \\ \alpha\beta F_k(1) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha F_k(1) & 0 & 0 & 0 & 0 \\ 0 & F_k(0) & 0 & 0 & 0 & F_k(0) & 0 \\ 0 & 0 & 0 & F_k(0) & 0 & 0 & F_k(0) \\ 0 & 0 & 0 & F_k(0) & 0 & 0 & F_k(0) \end{pmatrix} \quad (k=i, i+1, \dots, j), \quad (28)$$

and the symbol "Trace", has, instead of the usual meaning of the Trace, the meaning that if a is given by

$$a = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{17} \\ a_{21} & a_{22} & \cdots & a_{27} \\ \vdots & \vdots & \ddots & \vdots \\ a_{71} & a_{72} & \cdots & p_{77} \end{pmatrix}$$

a_{ij} 's being matrices of the same degrees as $F(\mu_i, \dots, \mu_j)$, then

$$\text{Trace} [a] = \sum_{k=1}^7 a_{kk}.$$

Eq. (26) with Eqs. (27) and (28) is the basic formula in the present calculation.

§ 4. Mean Dimension

In this section we proceed to calculate the mean square end-to-end distance of a polypeptide molecule. We denote the peptide (carbonyl) carbon atom, the asymmetric carbon

atom, and the peptide nitrogen atom of the i th residue by C_{3i-2} , C_{3i-1} and N_{3i} , respectively (See Fig. 2(a)). The vectors from N_{3i-3} to C_{3i-2} , from C_{3i-2} to C_{3i-1} , and from C_{3i-1} to N_{3i} are represented by r_{3i-2} , r_{3i-1} and r_{3i} , and their lengths by b_1 , b_2 and b_3 , respectively. The supplements of the valence angles, $\angle N_{3i-3}C_{3i-2}C_{3i-1}$, $\angle C_{3i-2}C_{3i-1}N_{3i}$ and $\angle C_{3i-1}N_{3i}C_{3i+1}$ are represented by ω_1 , ω_2 and ω_3 , respectively. We assume b_1 and ω_1 , etc., to remain unchanged in the helix-coil transition region. As in the previous articles¹³⁾, we choose a set of Cartesian coordinate systems attached to skeletal atoms as follows. The positive direction of x_{3i} axis of the i th coordinate system attached to C_{3i-1} coincides with r_{3i} , that of y_{3i} axis makes an acute angle with r_{3i-1} in the plane involving r_{3i-1} and r_{3i} and z_{3i} axis constitutes a right-handed rectangular coordinate system with x_{3i} and y_{3i}

axes. θ_{3i} is the angle between the two planes involving r_{3i-1} and r_{3i} and r_{3i} and r_{3i+1} , respectively. It is measured from the *trans* position to the direction of a clockwise rotation of r_{3i+1} , facing to the direction of r_{3i} (See Fig. 2(b)). Other coordinate systems also may be defined analogously.

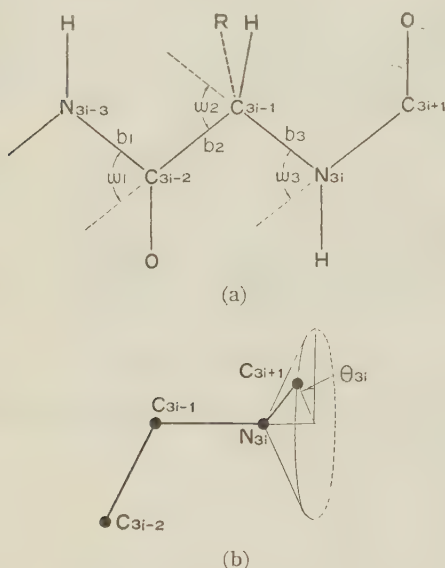


Fig. 2. Geometry of a polypeptide molecule, (a) bond lengths and supplements of bond angles; (b) rotational angles around skeletal bonds.

Here, it should be noted that the partition function, of course, can be expressed in the form of an integral by using the parameters defined above, provided that the contribution from side groups is suitably averaged. However, it is easily shown that the partition function of this form can be reduced to Eq. (2), if the range of integration on (for example) θ_{3i} is divided into two regions, a narrow one in which θ_{3i} is assumed to occur when the i th residue is *distorted*, and the rest, and thereafter the integration involved is performed. In this procedure we can find that the neglect of the sequences, 010 and 0110, are allowable when the former region is sufficiently narrow, which is just the case for the present problem.

Now the vector from N_{3i-3} to N_{3i} , $R_i = r_{3i-2} + r_{3i-1} + r_{3i}$, is given in the $(3i-2)$ th coordinate system by¹³⁾

$$R_i = b_1 + A(\theta_{3i-2}, \omega_1)b_2 + A(\theta_{3i-2}, \omega_1)A(\theta_{3i-1}, \omega_2)b_3, \quad (29)$$

where

$$b_1 = (b_1 0 0)^T, \quad b_2 = (b_2 0 0)^T \quad \text{and} \quad b_3 = (b_3 0 0)^T, \quad (30)$$

and

$$A(\theta, \omega) = \begin{pmatrix} \cos \omega & \sin \omega & 0 \\ \sin \omega \cos \theta & -\cos \omega \cos \theta & \sin \theta \\ \sin \omega \sin \theta & -\cos \omega \sin \theta & -\cos \theta \end{pmatrix}. \quad (31)$$

Then the scalar products, $R_i \cdot R_j$ and R_i^2 , are given by

$$\begin{aligned} R_i \cdot R_j = & \{ [b_3 A(\theta_{3i}, \omega_3) + b_2 A(\theta_{3i-1}, \omega_2) A(\theta_{3i}, \omega_3) \\ & + b_1 A(\theta_{3i-2}, \omega_1) A(\theta_{3i-1}, \omega_2) A(\theta_{3i}, \omega_3)] \\ & \times A(\theta_{3i+1}, \omega_1) \cdots A(\theta_{3j-3}, \omega_3) \\ & \times \{ b_1 E + b_2 A(\theta_{3j-2}, \omega_1) \\ & + b_3 A(\theta_{3j-2}, \omega_1) A(\theta_{3j-1}, \omega_2) \} \}_{1,1}, \quad (32) \end{aligned}$$

$$\begin{aligned} R_i^2 = & [(b_1^2 + b_2^2 + b_3^2)E + 2b_1 b_2 A(\theta_{3i-2}, \omega_1) \\ & + 2b_2 b_3 A(\theta_{3i-1}, \omega_2) \\ & + 2b_1 b_3 A(\theta_{3i-2}, \omega_1) A(\theta_{3i-1}, \omega_2)]. \quad (33) \end{aligned}$$

First we wish to average $R_i \cdot R_j$ and R_i^2 of a polypeptide molecule with specified μ_i 's over all possible ranges of $\theta_1, \theta_2, \dots, \theta_{3N}$. For the sake of simplicity, we assume that all rotations around skeletal bonds, though being hindered, are independent of each other. This assumption is indeed insufficient because of various steric hindrances between atoms^{13,14)} but it probably brings no serious error, so far as the present problem is concerned, since we take interest rather in a conspicuous change in the mean dimension, etc., in the transition region than in the absolute value of the mean dimension of a randomly coiled chain or its delicate temperature dependence. We may obtain a somewhat better approximation by assuming that the rotations around the two consecutive bonds, which together join the asymmetric carbon atom of a residue to the rest of the molecule, correlate with each other, but are independent of those around other bonds. This approximation would be better than a similar approximation proposed for vinylic molecules, because the correlation between rotations around the two bonds, the skeletal C-C bond of a residue and the C-N bond of the preceding residue along the chain (see Fig. 1), seems not to be very strong due to the planarity of the peptide C-C-N-C linkage, which prohibits, to some extent, for atoms of the two residues to become overcrowded. So far as we take into account the interaction between the rotations around first

neighboring bonds, the solidity of peptide linkages has the effect of separating all remaining bonds into many pairs of two consecutive bonds, of which the rotation around one bond interacts with that around another bond in the same pair but is independent of those around all other bonds belonging to different pairs. The procedure required for this approximation is straightforward, and, hence, is omitted here.

Under the assumption of the independent rotation mentioned above, each matrix appearing in scalar products can be averaged independently. We define the average of $A(\theta_{3i+k-3}, \omega_k)$ by

$$\langle A(\theta_{3i+k-3}, \omega_k) \rangle = A_{\mu_i, k}, \quad (k=1, 2, 3; i=1, \dots, N), \quad (34)$$

and, further, from these

$$A_{\mu_i} = A_{\mu_i, 1} A_{\mu_i, 2} A_{\mu_i, 3}, \quad (i=1, \dots, N) \quad (35)$$

Averaging $R_i \cdot R_j$ and R_i^2 by using Eqs. (34) and (35), and last, averaging over all possible values of μ_i 's by using Eq. (26), we obtain

$$\langle R_i \cdot R_j \rangle = [\text{Trace} \{ Q_* Y A^{j-i-1} Z \}]_{1,1}, \quad (36)$$

and

$$\langle R_i^2 \rangle = [\text{Trace} \{ Q_* X \}]_{1,1}, \quad (37)$$

where A , X , Y and Z are given by

$$H = (1/\lambda) \begin{pmatrix} \alpha\beta H_1 & 0 & 0 & 0 & \alpha H_1 & 0 & 0 \\ 0 & 0 & \alpha H_1 & 0 & 0 & 0 & 0 \\ \alpha\beta H_1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha H_1 & 0 & 0 & 0 & 0 \\ 0 & H_0 & 0 & 0 & 0 & H_0 & 0 \\ 0 & 0 & 0 & H_0 & 0 & 0 & H_0 \\ 0 & 0 & 0 & H_0 & 0 & 0 & H_0 \end{pmatrix}, \quad (38)$$

$$H = A, X, Y \text{ and } Z,$$

with

$$X_\mu = (b_1^2 + b_2^2 + b_3^2)E + 2b_1 b_2 A_{\mu,1} + 2b_2 b_3 A_{\mu,2} + 2b_1 b_3 A_{\mu,1} A_{\mu,2}, \quad (39)$$

$$Y_\mu = b_3 A_{\mu,3} + b_2 A_{\mu,2} A_{\mu,3} + b_1 A_{\mu,1} A_{\mu,2} A_{\mu,3}, \quad (40)$$

and

$$Z_\mu = b_1 E + b_2 A_{\mu,1} + b_3 A_{\mu,1} A_{\mu,2}. \quad (41)$$

Introducing Eqs. (36) and (37) into

$$\langle R^2 \rangle = \sum_{i=1}^N \langle R_i^2 \rangle + 2 \sum_{1 \leq i < j \leq N} \langle R_i \cdot R_j \rangle,$$

we obtain

$$\langle R^2 \rangle = [\text{Trace} \{ Q_* \{ NX + 2Y((N-1)E - NA + A^N)(E-A)^{-2}Z \} \}]_{1,1}. \quad (42)$$

If we wish to cover all cases, from the perfect helix to a randomly coiled chain for a polypeptide molecule with a given degree of polymerization, we must take into account all terms in Eq. (42). However, it seems impossible to diagonalize the matrix A and, hence, also to calculate A^N . When the molecular chain has some flexibility or involves some amount of randomly coiled sections, Eq. (42) becomes, in the limit of $N \rightarrow \infty$,

$$\langle R^2 \rangle / N = [\text{Trace} \{ Q_* \{ X + 2Y(E-A)^{-1}Z \} \}]_{1,1} \quad (43)$$

The expression for the α -helix will be given later. In the present theory we have neglected any long-range interaction between residues. Most of solvents in which the transition occurs have very high solubility power even for the polypeptide molecules with no charged group, as seen, for example, in the high power in the Mark-Houwink equation for the molecular weight dependence of intrinsic viscosity¹¹. Therefore, polypeptide molecules expand considerably from their unperturbed dimensions. This situation is even more remarkable for the polypeptide molecules with charged groups, between which the long-range electrostatic repulsion acts. These long-range interactions, which seem not to be affected strongly by such a small change in atomsphere as is required to complete the helix-coil transition, may be roughly taken into account by the introduction of some proper assumptions, for example, that all randomly coiled sections, irrespective of numbers of residues which they contain, expand by the same degree as the perfect random coil does. More detailed inspections of these effects are beyond the purpose of the present work.

Now let the matrix T be given by

$$T = \{ T_{kl} \} = (E - A)^{-1} \quad (44)$$

where T_{kl} 's are matrices of three degrees. It is easily found that Eq. (44) may be written in the alternative form

$$\left. \begin{aligned} T_{k1} \{ E - (\alpha\beta/\lambda) A_1 \} - T_{k3} (\alpha\beta/\lambda) A_1 &= \delta_{k1} E, \\ T_{k2} - T_{k5} (1/\lambda) A_0 &= \delta_{k2} E, \\ T_{k3} - (T_{k2} + T_{k4}) (\alpha/\lambda) A_1 &= \delta_{k3} E, \\ T_{k4} - (T_{k6} + T_{k7}) (1/\lambda) A_0 &= \delta_{k4} E, \\ T_{k5} - T_{k1} (\alpha/\lambda) A_1 &= \delta_{k5} E, \\ T_{k6} - T_{k5} (1/\lambda) A_0 &= \delta_{k6} E, \\ T_{k7} \{ E - (1/\lambda) A_0 \} - T_{k6} (1/\lambda) A_0 &= \delta_{k7} E, \end{aligned} \right\} \quad (k=1, 2, \dots, 7), \quad (45)$$

δ_{kl} being the Kronecker's delta. By solving this set of linear matrix equations we can obtain all T_{kl} 's, which are not displayed here to save space. Introducing these, and u_i 's and v_i 's given by Eq. (17) and (18) into Eq.

(43), we find

$$\langle R^2 \rangle / N = [\xi X_1 + (1 - \xi) X_0 + 2\{Y_1 S_{11} Z_1 + Y_1 S_{10} Z_0 + Y_0 S_{01} Z_1 + Y_0 S_{00} Z_0\}]_{1,1}, \quad (46)$$

where

$$\left. \begin{aligned} S_{11} &= c\{A_1^{-3} + (1 - \alpha\beta/\lambda)(A_1^{-1} + A_1^{-2})\}K\{A_1^{-3} + (1 - \alpha\beta/\lambda)(A_1^{-1} + A_1^{-2})\} \\ &\quad - (A_1^{-1} + A_1^{-2} + A_1^{-3}) - (1 - \alpha\beta/\lambda)(2A_1^{-1} + A_1^{-2}), \\ S_{10} &= c(\lambda - \alpha\beta)\{A_1^{-3} + (1 - \alpha\beta/\lambda)(A_1^{-1} + A_1^{-2})\}K(\lambda E - A_0)^{-1}, \\ S_{01} &= c(\lambda - \alpha\beta)(\lambda E - A_0)^{-1}K\{A_1^{-3} + (1 - \alpha\beta/\lambda)(A_1^{-1} + A_1^{-2})\}, \\ S_{00} &= c(\lambda - \alpha\beta)(\lambda - 1)^{-1}\{A_1^{-3} - (\alpha\beta/\lambda)A_1^{-2} + (\alpha^3\beta/\lambda^3)E\}K(\lambda E - A_0)^{-1}. \end{aligned} \right\} \quad (47)$$

with

$$K = \{A_1^{-3} - (\alpha\beta/\lambda)A_1^{-2} - (\alpha^3\beta/\lambda^3)A_0(\lambda E - A_0)^{-1}\}^{-1}. \quad (48)$$

When α becomes zero, β being finite, then $\lambda \rightarrow 1$, $\xi \rightarrow 0$, $K \rightarrow A_1^{-3}$, S_{11} , S_{10} , $S_{01} \rightarrow 0$, and $S_{00} \rightarrow (E - A_0)^{-1}$. Hence, Eq. (46) reduces to

$$\langle R^2 \rangle / N = [X_0 + 2Y_0(E - A_0)^{-1}Z_0]_{1,1}, \quad (49)$$

which is the expression for a randomly coiled chain.

We proceed to calculate the end-to-end distance of the α -helix, R , which is simply equal to N times of the pitch per residue. If we assume a unit vector along the molecular axis of the α -helix to be given by $\nu = (\nu_x \nu_y \nu_z)^T$, ($\nu_x^2 + \nu_y^2 + \nu_z^2 = 1$), in the $(3i+1)$ th coordinate system, it should be given by $A_1 \nu$ in the $(3i-2)$ th coordinate system. Since all residues in the α -helix are equivalent, $A_1 \nu$ should be equal to ν , i.e.,

$$(E - A_1)\nu = 0. \quad (50)$$

Since the matrix A_1 , which represents an orthogonal transformation, has the eigenvalue, unity, Eq. (50) has a nontrivial solution. Further, since A_1 is not the unit matrix, ν can be determined uniquely. The component of R_i along the direction of the molecular axis is equal to the pitch and, hence, we obtain

$$R = N|\nu^T\{b_1 + A_{1,1}b_2 + A_{1,1}A_{1,2}b_3\}|. \quad (51)$$

When the configuration of a polypeptide molecule becomes very near the α -helix, or the largest eigenvalue of the matrix A approaches very near unity, Eq. (46) ceases to be valid. Some appropriate interpolation formula, which is valid in this region, is required.

§ 5. Electric Moment

Recently, Wada¹⁶⁾ has reported that the

electric moment of poly- γ -benzyl-L-glutamate in ethylenedichloride is very large and changes linearly with the degree of polymerization, as can be anticipated. Consequently, it seems worthwhile to discuss the electric moment. Let the electric moment vector of the i th residue have the components, $u_{\mu_i, x}$, $u_{\mu_i, y}$ and $u_{\mu_i, z}$ in the $(3i-2)$ th coordinate system. From these we define

$$u_{\mu_i}^2 = u_{\mu_i, x}^2 + u_{\mu_i, y}^2 + u_{\mu_i, z}^2. \quad (52)$$

Then similarly, we obtain

$$\langle u^2 \rangle = [\text{Trace}\{Q_*\{NU + 2V((N-1)E - NA + A^N)(E - A)^{-2}W\}\}]_{1,1}, \quad (53)$$

where U , V and W are given by Eq. (38) with

$$U_\mu = d_\mu^T d_\mu, \quad (54)$$

$$V_\mu = d_\mu^T A_\mu, \quad (55)$$

and

$$W_\mu = d_\mu = \begin{pmatrix} u_{\mu, x} & 0 & 0 \\ u_{\mu, y} & 0 & 0 \\ u_{\mu, z} & 0 & 0 \end{pmatrix}. \quad (56)$$

When the molecular chain has some flexibility, Eq. (53) reduces to, in the limit of $N \rightarrow \infty$,

$$\langle u^2 \rangle / N = [\xi U_1 + (1 - \xi) U_0 + 2\{d_1^T A_1 S_{11} d_1 + d_1^T A_1 S_{10} d_0 + d_0^T A_0 S_{01} d_1 + d_0^T A_0 S_{00} d_0\}]_{1,1}. \quad (57)$$

When α becomes zero, β being finite, Eq. (57) reduces to

$$\langle u^2 \rangle / N = [d_0^T (E + A_0)(E - A_0)^{-1} d_0]_{1,1}. \quad (58)$$

As for the electric moment of the α -helix, the components perpendicular to the molecular axis cancel each other, but those parallel to the axis are left unvanishing. Thus the expression for the α -helix becomes

$$u = N|\nu^T u_1|. \quad (59)$$

Acknowledgement

The author wishes to thank Mr. T. Kotaka and Mr. A. Teramoto for their useful discussions and assistances in preparation of the manuscript. The author wishes to acknowledge several illuminating discussions of this problem with Dr. A. Wada. Thanks are tendered to the Ministry of Education of the Japanese Government for a grant-in-aid.

Appendix

In this appendix we wish to construct a partition function including various effects such as the end effect, the influence of a degree of polymerization, etc. Considering the specific contribution from each residue of a molecule to the partition function, we find that it is convenient to divide all residues into the following three groups: the first residue with a free carboxyl group, the N th residue with a free amino group, and the rest put between them. As for the third group, we assume the contributions to the partition function from the middle residues of the sequences, 111, 101, 011, 001, 110, 100 and 000, to be $\alpha\beta$, γ_3 , α_2 , γ_1 , α_1 , γ_2 , and 1 respectively. Then the matrix associated with these residues is given by, instead of Eq. (4),

$$p = \begin{pmatrix} \alpha\beta & 0 & 0 & 0 & \alpha_1 & 0 & 0 \\ 0 & 0 & \alpha_2 & 0 & 0 & 0 & 0 \\ \alpha\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha_2 & 0 & 0 & 0 & 0 \\ 0 & \gamma_3 & 0 & 0 & 0 & \gamma_2 & 0 \\ 0 & 0 & 0 & \gamma_1 & 0 & 0 & 1 \\ 0 & 0 & 0 & \gamma_1 & 0 & 0 & 1 \end{pmatrix} \quad (\text{A-1})$$

where β is the contribution from a hydrogen bond, as in the text. The eigenvalue equation of this matrix is found to be

$$\lambda^3(\lambda - \alpha\beta)(\lambda - 1) - \alpha\alpha_1\alpha_2\beta\{\gamma_3(\lambda - 1) + \gamma_1\gamma_2\} = 0. \quad (\text{A-2})$$

Further, we assume the contribution from the first residue, which can never be involved in a helical section, to be γ_c' when the second residue is *distorted*, or γ_c when it is *undistorted*. Then the matrix associated with this residue, p_c , can be obtained from p by substituting γ_c' for γ_1 and γ_c for 1 (in the seventh row) and making all remaining elements zero. Similarly, the matrix associated with the N th residue, p_a , can be obtained from p by sub-

stituting γ_a' for γ_2 and γ_a for 1, and making all remaining elements zero. The meaning of γ_a' and γ_a is now self-evident. Some additional contributions from the three NH and three CO groups which are located at both ends of a helical section can be taken into account through γ_1 , γ_2 , γ_3 , γ_c' and γ_a' .

Now the partition function is given by

$$Z = \text{SAE}[p_c p^{N-2} p_a], \quad (\text{A-3})$$

where the symbol "SAE" means the sum of all elements of the matrix. Provided that λ_k ($k=1, 2, \dots, 5$) is the eigenvalue of p , and u_k and v_k are the corresponding right-hand side and left-hand side eigenvectors, respectively, and they are normalized as $v_k u_k = 1$, p^{N-2} can be expanded in the form

$$p^{N-2} = \sum_{k=1}^5 \lambda_k^{N-2} u_k v_k. \quad (\text{A-4})$$

Introducing Eq. (A-4) into Eq. (A-3) and performing the calculation involved, we obtain

$$\begin{aligned} Z = & 2\alpha\alpha_1\alpha_2\beta \sum_{k=1}^5 \lambda_k^{N-2} (\lambda_k - 1) \\ & \times \{\gamma_c' + \gamma_1\gamma_c(\lambda_k - 1)^{-1}\} \{\gamma_a' + \gamma_2\gamma_a(\lambda_k - 1)^{-1}\} \\ & \times \{5\lambda_k^4 - 4(1 + \alpha\beta)\lambda_k^3 + 3\alpha\beta\lambda_k^2 - \alpha\alpha_1\alpha_2\beta\gamma_3\}^{-1}. \end{aligned} \quad (\text{A-5})$$

Note added in proof:

We can derive a less rigorous but more tractable expression for the mean square end-to-end distance by using a simplified model. In this model a helical section is replaced by a rod of $q_1 l_1$ in length if it contains q_1 residues and a randomly coiled section is replaced by random flight chain of q_0 rods of l_0 in length if it contains q_0 residues, and they are combined alternatively at the ends by a universal joint so as to form a interrupted helix. Applying the method described in the text for this model we can find the expression

$$\begin{aligned} \langle R^2 \rangle / N l_0^2 \\ = 1 - \xi + [\xi + 2c\{3 + (\beta/\alpha)\lambda(\lambda - 1)\}](l_1/l_0)^2. \end{aligned}$$

References

1. P. Doty, A. M. Holtzer, J. H. Bradbury and E. R. Blout: J. Amer. Chem. Soc. **76** (1954) 4493.
2. P. Doty and J. T. Yang: J. Amer. Chem. Soc. **78** (1956) 498.
3. P. Doty, A. Wada, J. T. Yang and E. R. Blout: J. Polymer Sci. **23** (1957) 851.
4. J. A. Schellman: Compt. rend. trav. Lab. Carlsberg, Ser. Chim. **29**, no. 15 (1955); J. Phys. Chem. **62** (1958) 1485.

- 5) S. A. Rice, A. Wada and E. P. Geidushek: Discussion Faraday Soc. **25** (1958) 130.
- 6) B. H. Zimm and J. K. Bragg: J. Chem. Phys. **28** (1958) 1246; **31** (1959) 526.
- 7) J. H. Gibbs and E. A. DiMarzio: J. Chem. Phys. **28** (1958) 1247; **30** (1959) 271.
- 8) S. A. Rice and A. Wada: J. Chem. Phys. **29** (1958) 233.
- 9) A. Miyake: Busseiron Kenkyu **2-4** (1958) 671.
- 10) M. B. Mathews, E. Kulonen and A. Dorfman: Arch. Biochem. Biophys. **52** (1954) 247. H. Boedtker and P. Doty: J. Amer. Chem. Soc. **78** (1956) 4267. P. J. Flory: J. Cellular Comp. Physiol. **49**, Suppl. 1 (1957) 175. J. M. E. Oth: Kolloid-Z. **162** (1956) 124.
- 11) J. Sturtevant, S. A. Rice and E. P. Geiduscheck: Discussions Faraday Soc. **25** (1958) 138.
- 12) H. A. Kramers and G. H. Wannier: Phys. Rev. **60** (1941) 252. E. N. Lassetre and J. P. Howe: J. Chem. Phys. **9** (1941) 747. E. W. Montroll: J. Chem. Phys. **9** (1941) 706.
- 13) K. Nagai: J. Chem. Phys. **30** (1950) 660; **31** (1959) 1169.
- 14) S. Lifson: J. Chem. Phys. **30** (1959) 964.
- 15) A. Wada: J. Chem. Phys. **29** (1958) 674; **30** (1959) 328, 329.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 3, MARCH, 1960

Proton Magnetic Resonance and X-Ray Diffraction Studies of Polypropylene*

By Atsuo NISHIOKA, Yasuhiro KOIKE, Masakazu OWAKI,
Tsunezo NARABA and Yoshinori KATO

*Electrical Communication Laboratory, Nippon Telegraph
and Telephone Public Corporation,
Musashino, Tokyo, Japan*

(Received May 11, 1959)

Crystallization and glass transition in various samples of polypropylene, have been studied by proton magnetic resonance over the wide temperature range $-180\sim 200^{\circ}\text{C}$, and by X-ray diffraction at room temperature. It was found that the free rotation of methyl groups would be hindered below -130°C and the second moment tended to increase towards the rigid state value. Motional narrowing occurs gradually at -40°C in atactic polymer which is mostly amorphous. On the other hand, isotactic polymer which is highly crystalline, showed rather sharp narrowing from -10°C to 30°C , but the condition of heat treatment affected the behaviors of narrowing. X-ray diffraction patterns suggest that quenched film has smaller size of crystallite than that of annealed film. The line shape of atactic polymer is very similar to that of amorphous component decomposed by Wilson-Pake method in isotactic polymer, and then the degree of crystallinity of highly crystalline isotactic sample was estimated about 70~80% at room temperature. When the isotactic polymer was cooled down from 200°C , recovery of crystallization was observed between 140 and 120°C .

§1. Introduction

It is very important to study the behaviors of crystallization in crystalline polymer, i.e., the changes of the degree of crystallinity with

temperature, the difference of crystallinity and size of crystallites by heat treatment, and the temperature range of crystallization etc., and also to know the molecular process of freezing of segmental motion through the behavior of polymer in the glass transition temperature region. Recently nuclear mag-

* Read at the 13th annual meeting of the Physical Society of Japan at Kyoto University in October, 1958.

netic resonance method is found to be very useful to study these subjects of crystallization and glass transition in crystalline polymer¹⁾.

In the present study some measurements by proton magnetic resonance and X-ray diffraction were carried out about the recently developed stereospecific polymer, polypropylene²⁾. This polymer usually obtained by the stereospecific catalyst is usually composed of three kinds of different steric configuration which are called isotactic, atactic, and stereoblock by Natta.³⁾ Isotactic polymer is a linear polymer with a complete head-to-tail ordered arrangement and with the monomer units all disposed in the same steric configuration along the polymer chain; atactic polymer is a linear polymer with a randomly ordered arrangement and does not possess a steric order of the monomer units; and stereoblock polymer is a linear polymer with a partially ordered arrangement and with partial sequence of steric ordered monomer units³⁾.

Recently the molecular motion of isotactic and atactic polypropylene polymers was investigated with interesting results by W. P. Slichter³⁾ and J. A. Sauer⁴⁾ by nuclear magnetic resonance and dynamic mechanical measurements. Our study was independently performed mainly about the effect of heat treatment upon crystallization, molecular motion near the glass transition temperature, crystal-

lization recovery of highly isotactic and stereoblock polypropylene.

§ 2. Materials

Several different samples of polypropylene have been studied. Most of them were originally the commercial products of Moplen M-2 manufactured by Montecatini Company. Natural Pellet and Natural Powder were used. From 5 grammes of Natural Powder extracted by toluene at 100°C for 40 hours, the extracts and residues were obtained. Another group of samples supplied through the courtesy of Professor Kambara and Mr. Oshika of Tokyo Institute of Technology, were extracted by ether and n-heptane. The extract of M-2 by ether was negligibly small in amount.

To study the effect of heat treatment, quenched and annealed films were molded by hot press at 180°C for 2 min. and then quickly immersed into dryice-methanol bath or annealed at 100°C or room temperature. The molded samples have usually light brown color, the cause of which is not yet made clear, but may be ascribed to either thermal decomposition through some weak bonds, residual catalyst or to other impurities. Some conditions of molding these samples are given in Table I with other remarks.

§ 3. Apparatus

The apparatus for studying nuclear mag-

Table I. Specifications of Polypropylene Samples Tested.

Sample No.	Thickness (mm)	Molding and after-treatment conditions	Original Material	Extraction
1	1.0	quenched into -65°C bath after molded at 180°C, 2 min.	Natural Pellet	None
2	1.0	annealed at 100°C, 1 hr after molded at 180°C, 2 min.	Natural Pellet	None
3	0.15	quenched like No. 1	Natural Powder	None
4	0.15	annealed like No. 2	Natural Powder	None
13	0.15	quenched like No. 1	Natural Powder	Toluene residue at 100°C, 40 hrs.
13'	0.15	annealed slowly from 200°C to room temperature	Natural Powder	same as No. 13
14	0.15	quenched like No. 1	Natural Powder	Toluene extract at 100°C, 40 hrs.
14'	0.15	annealed like No. 13'	Natural Powder	same as No. 14
250-E & 252-E	—	—	Polymerized by Prof. Kambara	Ether extract
252-H	1.6	slowly solidified from 150°C	Kambara	N-heptane extract after extracted by ether

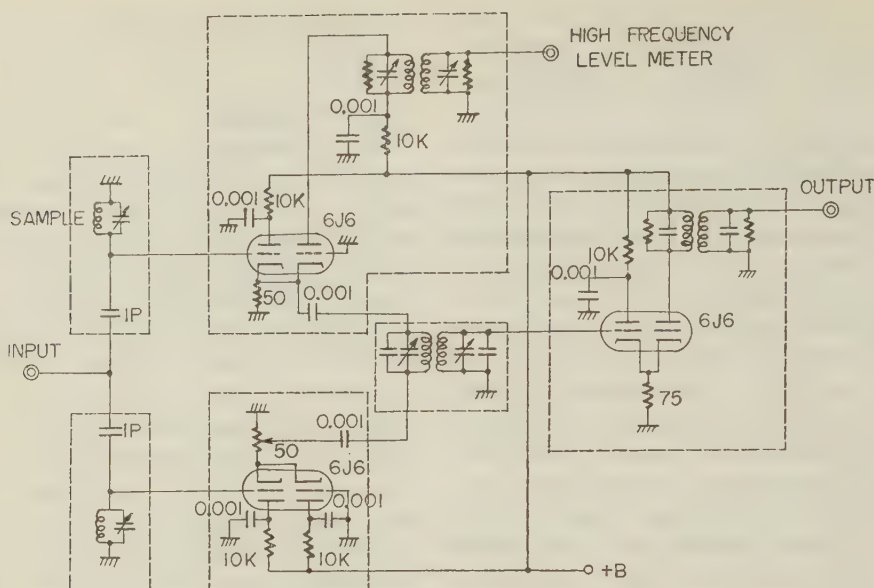


Fig. 1. Bridge circuit.

netic resonance was constructed and assembled by Koike, the main parts of which are 30 Mc/s oscillator multiplied by 100 kc/s quartz oscillator, balanced tube type bridge (Fig. 1), phase sensitive detector, temperature controlled modified Gutowsky type cryostat, highly stabilized electromagnet.

X-ray diffraction study was carried out by the use of conventional Geiger counter type spectrometer.

§4. Comparison of Crystalline Characters of Various Samples by X-ray Diffraction

Since there may be expected some differences in their crystalline characters among various samples, their X-ray diffraction patterns were recorded as shown in Figs. 2, 3 and 4.

At first, using Cu target, samples No. 1~No. 4 were compared. As seen from Fig. 2 (a) and (b), the quenching treatment in No. 1 seems to be not so effective compared with No. 2. Perhaps the thickness of 1 mm in this samples would be too large to detect the effect of heat treatment. Although the surface of No. 1 was quenched, its interior would be annealed, and after all the contributions from the annealed part would be larger than the quenched one. Then we have molded thinner films, No. 3 and No. 4, which show large differences in their diffraction patterns as shown in Fig. 2(c) and (d). Since the differ-

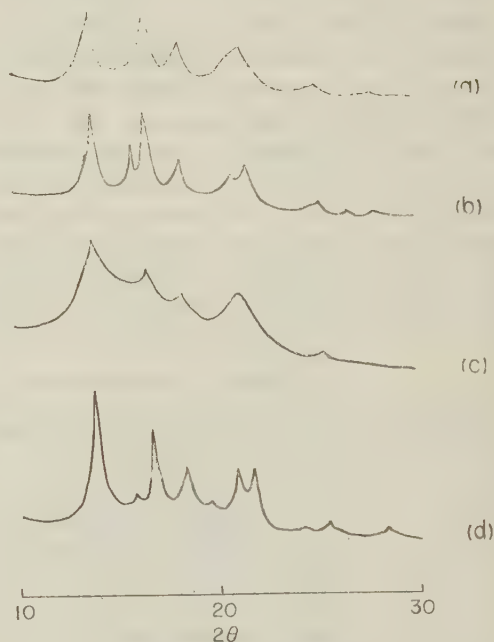


Fig. 2. X-ray diffraction patterns of polypropylene films (a) No. 1 (b) No. 2 (c) No. 3 (d) No. 4.

ences in their diffraction patterns will be caused by the difference of their size of the crystallites, slowly scanned patterns were recorded using Co $K\alpha$ as shown in Fig. 3(a) and (b) to separate the peaks more clearly. Then using Scherrer's formula, the size of the crystallites were roughly estimated.

$$D = k\lambda / \beta \cos \theta,$$

where D is the size of the crystallite ($\text{\AA}$), λ the wave length ($\text{\AA}$), β the half-height width in angle, and θ the Bragg angle. We have chosen k as 0.9, and λ is $1.787 \text{ \AA}$ for Co $K\alpha$. Correcting the width due to the apparatus and the width of non-separable α_1 and α_2 , corrected half-height width is obtained. The contribution from the former correction appeared even in single crystal cannot be neglected in small angle patterns, while the latter can be. Here, MoS_2 ($2\theta = 16^\circ$) was used as the standard sample. Then D was obtained as 150 and 200 $\text{\AA}$ from the smaller angle two peaks in No. 3 and 230 and 280 $\text{\AA}$ in No. 4. Thus, it was confirmed that quenching is more effective in growing smaller size crystallites than annealing. The estimation of these D values are rather rough, but their order of magnitude seems to be plausible, judging from the comparison with D values in polyethylene.

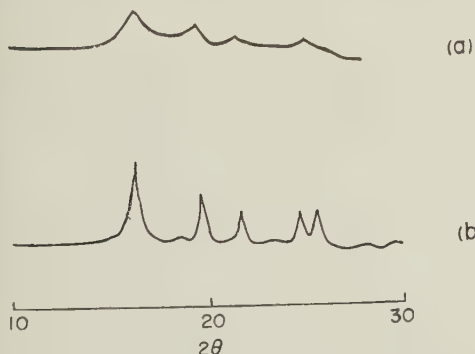


Fig. 3. X-ray diffraction patterns of polypropylene films (a) No. 3 (b) No. 4.

Although above samples were all molded from M-2, we can see more distinct differences in crystalline character by comparing other samples in Fig. 4. No. 13', toluene residue, which is highly isotactic and crystalline, shows rather similar but slightly more crystalline character than No. 4. On the other hand, the pattern of 252-E which is extracted by ether, suggests highly amorphous character of this sample. There can be observed some small peak, but it is not clear whether this is due to the existence of isotactic molecules of lower molecular weight, or to the coexistence of both isotactic segment crystallizable and atactic segment in the same molecule. But this pattern seems

to be consistent with the assumption that ether extract is considered as almost atactic and amorphous sample.

The n-heptane extract (252-H) and toluene extract (No. 14) are both supposed to contain so-called stereoblock polymer⁵⁾, but remembering that toluene has higher boiling point than n-heptane, there may still remain some possibility of assuming that the toluene extract has some fraction of isotactic polymer of low molecular weight which is larger than that of 252-H. These differences may suggest higher crystallinity in No. 14 than 252-H, but as seen from Fig. 4(a) and (d) the actual situation seems to be the opposite. Presumably this fact may be attributable to the differences in their heat treatment; No. 14 was quenched at room temperature after molded at 180°C for 2 min., whereas 252-H was slowly solidified in the holder of X-ray diffractometer after melted at 150°C . These different treatment may suggest that the former is slightly quenched and the latter is annealed, and thus we can expect higher crystalline behavior in 252-H than No. 14.

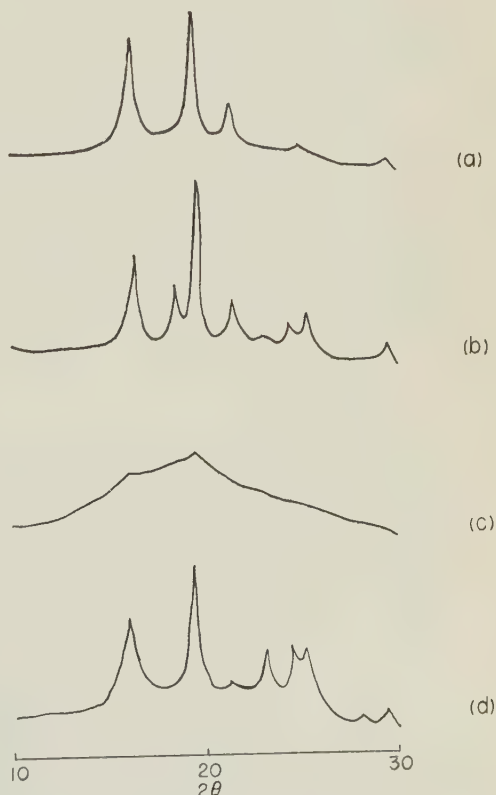


Fig. 4. X-ray diffraction patterns of polypropylene (a) No. 14 (b) No. 13' (c) 252-E (d) 252-H.

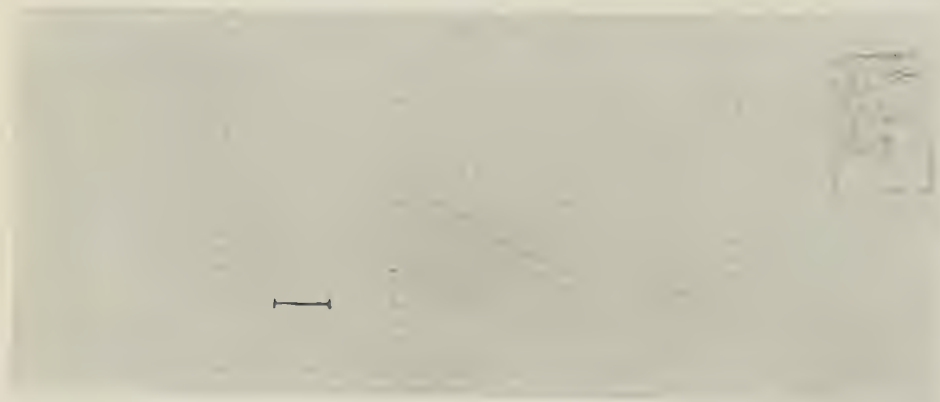
The different characters of crystalline state in various samples above mentioned will be helpful to discuss the following results by nuclear magnetic resonance absorption.

§ 5. Proton Magnetic Resonance Study

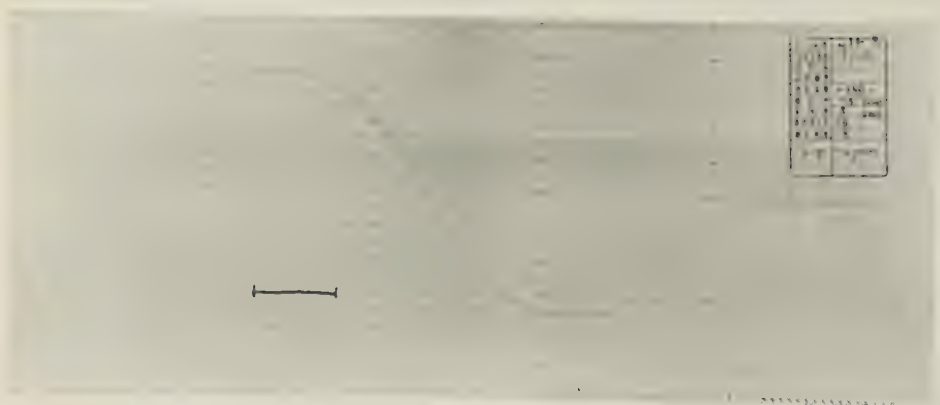
5.1. Line shape

Typical line shapes are shown in Fig. 5. From -50 to -10°C the line shapes of these

samples, except the atactic and toluene extracts, are almost the same with each other, and are simple bell shape. Especially below -40°C there are no significant difference between atactic and isotactic polymers. Further cooling below -130°C , makes the line shape more flat with plateau. As will be mentioned later, these broadening contributes the increase of second moment more than 10 gauss² which



(a) No. 4, -180°C



(b) No. 4, -150°C



(c) No. 1, -24°C

is reasonable ascribed to the freezing of the rotation of methyl groups.

Above -40°C there are significant differences in the line shape between the extracts and other non-extract samples. The motional narrowing occurs at lower temperatures in the former than in the latter, which has almost the same shape below -10°C . From

-10 to 30°C the effect of heat treatment can be observed, and there appears narrow part in the derivative curves, which increases rapidly with increasing temperature, superimposed by the broad part like the well known Wilson-Pake type⁶⁾. It might be concluded that in higher temperatures the broad tail in the extracted sample, especially 250-E, at room

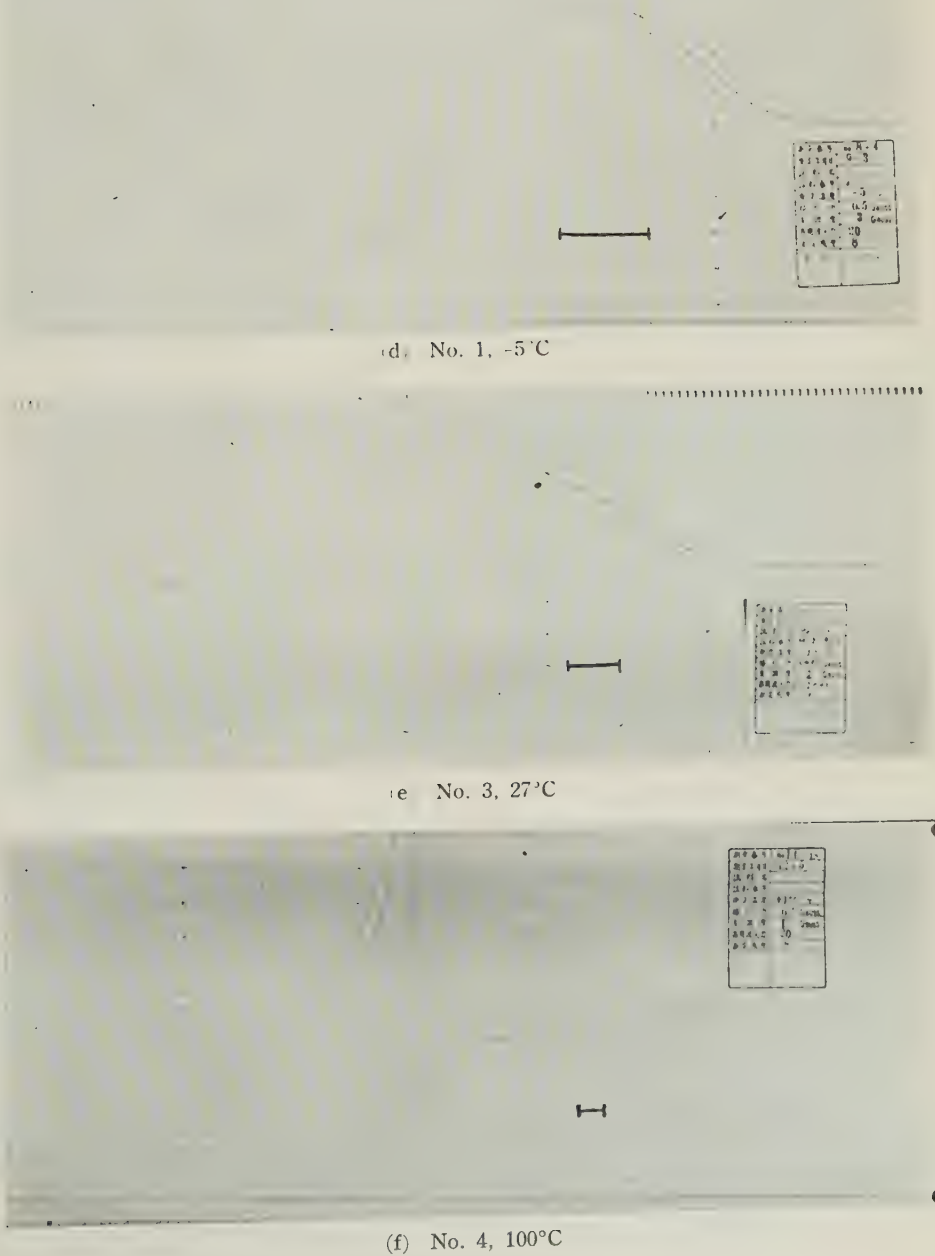


Fig. 5. Line shapes of Moplen M-2 at Various Temperatures.

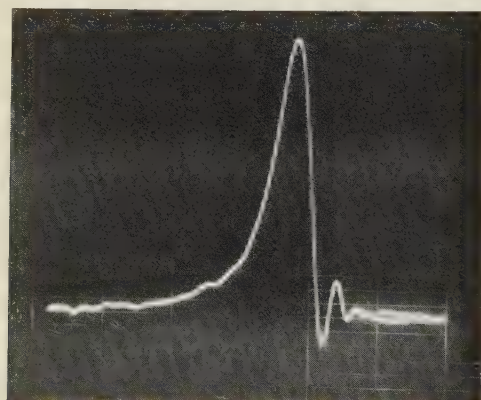
temperature will disappear, whereas in other crystalline samples there remains the broad tail even at higher temperatures. From these rather different behaviors in those two kinds of samples, and remembering the X-ray diffraction pattern of 252-E, it would be suggested that 250-E might be considered to be almost atactic and amorphous. And the fact that all the crystalline samples show almost the same shape below -40°C , would suggest that this shape may give the rigid state line shape of crystalline part of polypropylene except the rotation of methyl groups. Therefore the room temperature curve of crystalline samples could be decomposed in two parts; one of which is the rigid state crystalline part and the other residual part may correspond to the amorphous one. This method enables us to estimate the degree of crystallinity of various crystalline samples.

Another fact to be mentioned is that the long tail can be observed in crystalline samples at rather high temperature near the melt-

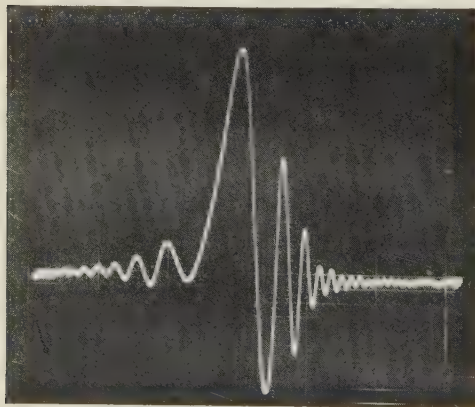
ing point about 175°C , which suggest the larger crystallites, to persist at such a high temperature. Above the melting point, wiggles can be observed in isotactic sample as seen from Fig. 6(a). Compared to this shape, 252-H in Fig. 6(b) shows rather intense wiggles at 170°C , which suggest the molecular motion to occur more easily in this sample. These results about resonance line shape and X-ray diffraction pattern in 252-H suggests that there can be some difference in molecular structure between 252-H and residue. The word "stereoblock" will be compatible with these results about 252-H.

5.2. Motional narrowing in line width

A typical example of line width narrowing in wide temperature range from -180 to 200°C is given in Fig. 7. A slight change of line width in maximum slope can be seen at lower temperatures, but at these lower temperatures $\Delta H_{m,sl}$ is very inaccurate, because the derivative curve show wider plateau. In this case, it is reasonable to estimate half-height width, $\Delta H_{1/2}$. Comparing the values of $\Delta H_{1/2}$ at -180°C and -15°C , their difference is only 2 gauss.



(a) No. 4, 180°C , modulation 30 c/s, 2.4 gauss.



(b) No. 14, 170°C , modulation 30 c/s, 2.4 gauss.

Fig. 6. Absorption curves at high temperatures.

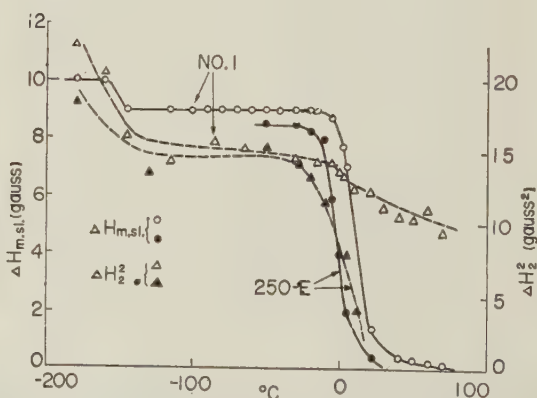


Fig. 7. Temperature dependence of line width and second moment of polypropylene.

The interesting line width transitions lie between -40°C and room temperature, and there are much differences in the behavior of motional narrowing between extracts and non-extracts. The former show only small difference between quenched and annealed samples, whereas toluene residue and natural samples show marked differences by heat treatment, suggesting the striking influences of crystallization upon the motional narrowing, and their onset of narrowing occurs ex-

clusively near -10°C .

As shown in Fig. 8, the tendency of narrowing with increasing temperature is more sharp in annealed samples than in quenched samples. At first sight it might be expected that the line width in maximum slope derived from the amorphous part in the derivative curve should be narrower in quenched sample than in annealed samples, if the sample would be composed of two phases, amorphous and crystalline, and two types of line shape, one narrow and the other broad, will correspond to each phase respectively. But, strictly speaking, the concept of two phases could not be applicable to crystalline which connect the crystallites and typical amorphous part, and are less labile than the ordinary amorphous region. These constrained amorphous regions would modify the contribution to the line width of narrow part in the derivative curve,

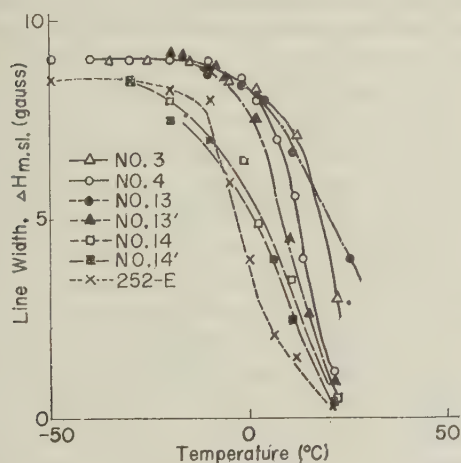


Fig. 8. Line width narrowing near second-order transition.

and broaden the width apparently. As seen from the preceding description, X-ray diffraction pattern suggest the existence of smaller sizes of crystallites in quenched sample than annealed one, and there is not so large difference in the degree of crystallinity in both samples. Therefore, the volume of the constrained amorphous part would be larger in the quenched sample than the annealed one, and this situation would perhaps explain the broadening of line width in quenched amorphous region. The residue sample is much more remarkable in this tendency than the non-extracted samples because there are contained much more isotactic polymers in the

former, and may be larger changes in the constrained amorphous volume due to the heat treatment. Another factor to be suggested is that the amorphous part in these samples may consist of non-crystalline atactic segment and amorphous isotactic segment, which possibly coexist in each large molecules, and the molecular motion will be different in both regions.

As for the glass temperature of this polymer, Natta⁷⁾ has already found that it was about -35°C and independent of the molecular stereospecificity of this polymer, i.e., isotactic, stereoblock, or atactic. In the first approximation, there would not be so much differences in the amorphous state of above structures, but in detailed consideration we shall expect different behaviors with respect to each other toward the glass transition. As described before, so-called "isotactic" polymer contains both atactic amorphous and isotactic amorphous parts in the macromolecules, and atactic polymer could be considered to be almost amorphous state, and the existence of isotactic amorphous state in isotactic polymer would suggest the different behavior near the glass transition. The onset of motional narrowing occurs near -40°C , which is very close to the glass temperature reported by Natta, and seems to be in close relation with the gamma peak temperature 235°K recently pointed by Sauer⁴⁾ in non-crystalline sample. In Fig. 1 of his paper, there is seen this sort of peak in lower crystalline sample, but the appearance is rather weak compared with amorphous sample, and moreover, highly crystalline sample does not show this peak clearly. Sauer has attributed this peak to the onset of small scale chain motion in the amorphous portions of the polymer, but if we take account of the detailed structure of amorphous part, it may be perhaps more plausible to say that this small scale chain motion will occur in the amorphous state of atactic structure more frequently.

Above the glass temperature, the onset of marked narrowing in line width will correspond to the glassy to rubbery transition, which accompany the large scale segmental motions. From the analysis of the data in this region in the familiar fashion, the activation energy for the segmental motion was

calculated to be 7.0 Kcal/mole. On the other hand, the analysis of the narrowing in No. 1, gives its value of about 13 Kcal/mole which is higher than that of atactic sample. This fact shows that the segmental motion is more hindered in the amorphous state of highly isotactic polymer by the presence of isotactic crystalline phase as suggested by Slichter. It also contains both isotactic amorphous state and atactic amorphous state as stated above. No. 14 and 252-H show the behavior which is similar to isotactic polymer in its crystallization, but is closer to atactic polymer in its molecular motion. This would suggest that the stereoblock polymer has amorphous parts mostly composed of atactic structure. The commercial sample contains about 10~15% of stereoblock polymer as mixture, but the crystallization and motional narrowing are rather close to those of isotactic or toluene residue.

5.3. Degree of crystallinity and crystallization temperature

In determining the degree of crystallinity by nuclear magnetic resonance method, it is necessary to confirm that the crystalline part does not show motional narrowing, and the amorphous part does show remarkable narrowing, and to perform this procedure safely it is better to select the temperature range, in which only the slight change of crystallinity is expected to occur. The changes of crystallinity with temperature was recently measured by infrared spectroscopy and dilatometry by Abe⁸⁾ and Nakane⁹⁾ respectively, who have shown slight changes of crystallinity in the temperature range from room temperature to about 100°C in highly crystalline polypropylene. On the basis of these results we can estimate the degree of crystallinity by NMR method in this temperature range. As shown in Fig. 9, the degree is about 70-80%, which shows rather high crystallinity of this polymer.

It may easily be expected that the polymer would crystallize at temperatures below the melting point after some interval of induction period* when cooling from the temperature

* It takes certain period of time for nuclei of crystallites to grow into sufficient extent in sizes and numbers detectable by means of the apparatus concerned. This time is usually called induction period.

above the melting point. Since the recrystallization was found by Abe⁸⁾ to occur near 130°C, we have tried to reexamine this behavior by nuclear magnetic resonance method. As it needs about 30 minutes to sweep the magnetic field in the resonance region, it is very difficult to obtain reliable results when the sweep interval is comparable to the induction period at some definite temperatures. As shown in Fig. 9, the appearance of broadening in the tail of the derivative curve can be seen very rapidly below about 140°C, and the whole shape of the curve recover at about 120°C. Considering the experimental error, it may be fairly well in accordance with both NMR and infrared analysis. The slightly higher values of crystallinity of cooled sample at room temperature may be attributable to the annealing effect encountered in the cooling process. In No. 14, there can be observed lower freezing temperature and lower degree of crystallinity as shown in Fig. 9.

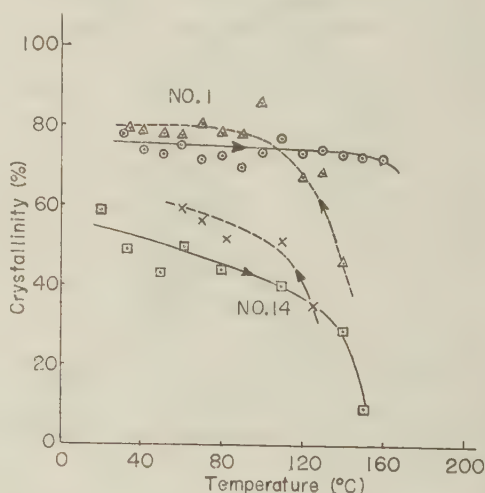


Fig. 9. Temperature dependence of crystallinity of polypropylene.

As suggested recently by Natta⁵⁾, the extract by n-heptane is considered to be a mixture of chain molecule which is constituted from alternatively arranged isotactic and atactic small segment in each molecule, that is, so-called "stereoblock" polymer. As easily expected from such a structure of stereoblock polymer, any isotactic segment in this polymer will find with less probability another isotactic segment of different molecule in arranging in its nearest neighbour than in highly isotactic polymer like residue from toluene. This tend-

ency would be ascribed presumably to lower crystallinity and smaller sizes of crystallites in stereoblock polymer than in the case of isotactic polymer. The smaller sizes of crystallites will lower the melting point of the polymer. These expectations are confirmed as seen from Fig. 9. In parallel to this experiment, infrared spectroscopic observation was done by Abe¹⁰, who showed that the behaviors in the hysteresis in crystallization is largely different among the three samples of isotactic, stereoblock, and atactic respectively. In ordinary crystalline polymer, the crystallization rate and the maximum crystallinity are higher in lower molecular weight sample than the higher as shown by Yamada¹¹ in polytrifluorochloroethylene. The lower rate and degree of crystallinity was observed in stereoblock polymer, which has lower molecular weight than isotactic sample. This opposite behavior of crystallization in the stereoblock polymer is reasonably consistent with the molecular structure, which have natural tendency to disturb the crystallization. If we interpret the word "stereoblock" generally, the isotactic and atactic are both the extreme cases, which are considered to be the ideal regular and irregular stereoblock respectively. The difference between the stereoblock and atactic may be as follows: the former may have smaller sizes of crystallites and lower crystallinity, but the latter may be almost perfectly amorphous, and expected to show no behavior of hysteresis in crystallization process as is the case in the former. As seen from Fig. 8, above mentioned expectation was confirmed in NMR data about 250-E. As expected from the characteristic feature of the polymerization process of this polymer, we may suppose that the molecular weight distribution of isotactic polypropylene would have the maximum position at higher molecular weight side, opposing the ordinary distribution of the polymer obtained by radical reaction, and so the extract by ether or acetone may have only small fraction of isotactic component of lower molecular weight.

Summarizing the results obtained in the toluene extract and n-heptane extract, they show the lower temperature for the onset of molecular motion than toluene residue and commercial samples, but almost the same with that of ether extract. The tendency of mo-

tional narrowing with increasing temperature is similar to that of ether extract. These behavior suggest that the structure of amorphous state in toluene and n-heptane extract is very similar to that of ether extract, that is, atactic structure. X-ray diffraction pattern of this sample shows rather crystalline nature, and similar to that of ordinary commercial sample though there are somewhat different characters. The degree of crystallinity and crystallization temperature are both lower than those of toluene residue and commercial samples, in spite of the lower molecular weight of these extracts than that of non-extracts. These behaviors suggest different crystallization mechanism in these extracts from that of ordinary crystalline homopolymer. If we presuppose the existence of the crystallization mechanism of recently proposed "stereoblock polymer", there should be lower probability of crystallization in neighbouring chain molecules, which causes lower crystallinity and lower crystallization temperature. As was suggested recently by Coleman¹⁹, the depression of crystallization temperature with cooling may give some measure of isotaxy. These characteristic features of toluene and n-heptane extracts are in good accordance with the concept of "stereoblock".

The toluene residue and commercial samples have higher temperature for the occurrence of segmental motion about -10°C . The tendencies of motional narrowing are different among quenched and annealed samples, suggesting the amorphous part to be somewhat different from that of extracts. The amorphous part of this sample will consist of atactic amorphous and isotactic amorphous chain segments, and these isotactic amorphous segments will vary in their content in the whole polymer sample, affected by heat treatment.

The degree of crystallinity is about 70~80% in ordinary molded sample at room temperature, and decreases slightly up to about 100°C . The melting point lies at about 170°C in Moplen M-2.

When cooling from the molten state, recrystallization occurs at about 140°C and recovers almost at about 120°C . This quick recovery of crystallization of this sample makes the quenching process difficult.

It is very difficult to determine the degree

of isotaxy in this polymer, but if we neglect the crystallization of atactic structure, the upper limit of the degree of crystallinity obtained from the well annealed sample at the crystallization temperature range would be at least the lower limit of isotaxy; in other words we might say that the degree of isotaxy would be larger than the degree of maximum crystallinity attainable in annealing process. Using this assumption the isotaxy of toluene residue may be more than 80%.

5.4. Second moment

Although the theory of Anderson¹²⁾ and Kubo-Tomita¹³⁾ predicts the invariance of second moment in the process of motional narrowing, observed second moments show usually decreasing with increasing temperature, because the long tail part comparable with noise are inevitably cutoff in obtaining the profile of derivative curve experimentally.

So, strictly speaking, the second moment has significant meaning only at the rigid state, but apparent decrease of its value is very useful in understanding the mechanism of motional narrowing of line width.

Fig. 7 shows the temperature dependence of observed second moment of No. 1 from -200 to 180°C , and other samples from -50 to 20°C . It is about 14 gauss^2 near -50°C , and $22\sim 26 \text{ gauss}^2$ near -180°C and tends to increase further at lower temperatures. These results are in fairly good accordance with those of Sauer⁴⁾ and Slichter³⁾.

To compare with this observed value, we have calculated the rigid state second moment. In the simplest case, we obtain the intramolecular contribution using tetrahedral bond angle and length as in the following.

$$22.5 \times 1/2 + 11.2 \times 1/3 = 15 \text{ gauss}^2.$$

The difference between this and the observed value, is about 10 gauss^2 , which is too large to be ascribed to the intermolecular contribution.

Recently Slichter³⁾ has calculated the rigid state second moment on the basis of Natta's helical structure of the isotactic polypropylene molecule¹⁴⁾, and found the intramolecular contribution to be 23.5 gauss^2 . But as he stated in his paper, there remains some ambiguity in the choice of the positions of three protons in CH_3 group about its rotational axis. His calculation is based on the model, which

brings two of the CH_3 group protons equally distant from the proton on the tertiary carbon in the next monomer on the helix, and gives minimum value about the interactions between the proton on the tertiary carbon and three protons of CH_3 group.

Generally speaking, this interactions should depend upon the relative positions of protons in this system. We have independently calculated this moment based upon Natta's helical structure, using tetrahedral bond angle and C-H distance of $1.094 \text{ \AA}$. As seen from Fig. 10, which is the projection on x - z plane containing any C-C-C on the main chain of helix, Slichter's model will correspond to the case of (a) in Fig. 10, and this gives the intramolecular contribution to ΔH_2^2 to be 25.6 gauss^2 slightly higher than Slichter's 23.5 gauss^2 , which is attributable to the smaller bond angle of tetrahedral C-C-C than the value 114° expected from the period of helix $6.5 \text{ \AA}$ in the unit cell at room temperature given by Natta.

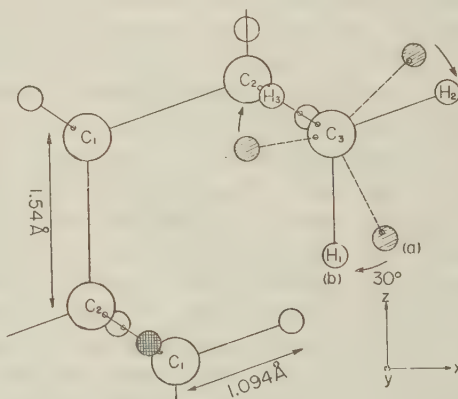


Fig. 10. Assumed positions of methyl group in the helix of polypropylene molecule.

On the contrary, if we choose the rest position of methyl group like (b) in Fig. 10, in which the protons of methyl group take the trans or gauche position against the proton of tertiary carbon on the same monomer unit, and so one of the C-H bond of CH_3 directs parallel to the axis of helix, the intramolecular contribution is found to be 26.6 gauss^2 , about 1 gauss^2 higher than in the case of (a). The distance between the proton on the tertiary carbon and the nearest neighbouring proton of CH_3 group are found to be 2.3 and $1.9 \text{ \AA}$ in the case of (a) and (b) respectively. The latter value seems to be rather

shorter than the distance expected from the ordinary van der Waals radius 2.4 Å. But as Powles¹⁵⁾ have already reported about polyisobutylene at lower temperatures, the interproton distance could take rather small value of 1.5 Å. Therefore the above value obtained would be permissible. Of course, since the free rotation of CH₃ group is considered to be hindered at lower temperatures, the shortest interproton distance given above would be excluded. Summarizing above descriptions, Slichter's data would give the minimum contribution to the second moment between CH proton and CH₃ protons, but because some rather short distances must be taken at lower temperatures, the intramolecular contribution to ΔH^2 would possibly be larger than Slichter's calculated value. So far as the stable position of CH₃ against CH in the same unit is concerned, the position in Fig. (b) is most plausible at low temperature, but the magnetic dipolar interaction between the CH₃ protons and CH proton on the tertiary carbon of next unit would be in favor of (a) and modify slightly the position of CH₃ from (b) toward (a), accompanied by higher activation energy. Therefore, the plausible position would be intermediate between these two cases.

From the increasing tendency of the second moment at lower temperatures, it cannot be concluded that the methyl group is rigid at liquid air temperature, but the large difference between the behavior at this temperature and at about -50°C would suggest the existence of severe hindrance for the rotation of methyl group at liquid air temperature.

Fig. 7 shows that the second moment decreases to about 14 gauss² at -130°C and is nearly constant throughout the further increase of the temperature up until near 0°C. If all the methyl group contained in this polymer will be free in axial rotation even in the crystalline state in this temperature range, the second moment should decrease about 9 gauss² by this effect only. The observed difference is slightly higher than this value, but we may suppose this difference to be mainly due to the contribution from the free rotation of methyl groups, together with the residual contribution from hindered rotation or torsional oscillation of methylene groups.

5.5. Synthesis of absorption curve

Since the absorption curve in two or three spin system is given analytically by Pake¹⁶⁾ and Andrew¹⁷⁾ respectively, the absorption curve can be synthesized as the superposed system composed of these simple spin systems, assuming no interaction between these spin systems, but this assumption would not be applicable in a strict sense because of large contribution from intramolecular interaction.

In obtaining the synthesised curve, there are two parameters that is, the interproton distance in CH₂ or CH₃, and the broadening parameter due to external spin system, which introduce some arbitrariness and ambiguities in final results. We have obtained the curve, superposing in the ratio of 2:3, two spin curve of dichloroethane and three spin curve of trichloroethane¹⁸⁾, but there was not so good accordance between calculated and experimental curves, and the decrease of half width due to CH₃ rotation is about 5 gauss in the calculation, but 2 gauss in the experiment. As stated in the previous section, CH₃ rotation seems not to cease perfectly even at liquid air temperature.

§ 6. Conclusions

Our experimental results above mentioned are summarized as in the following.

- 1) Methyl groups do not appear to cease the rotation perfectly even at liquid air temperature, and seems to be in free rotation above -130°C.

- 2) The glass transition temperature seems to lie at about -40°C in ether extract (almost atactic) and toluene extract (almost stereoblock), but in toluene residue and commercial sample will be somewhat higher because the onset of molecular motion occurs at about -10°C in these highly crystalline sample (highly isotactic).

- 3) The ether extract has lower activation energy for segmental motion, and very low crystallinity. These behaviors suggest the almost amorphous character of this sample, which is in good accordance with the idea of "atactic polymer".

- 4) The toluene extract and *n*-heptane extract have intermediate structure between atactic and isotactic molecule, which is in good accordance with the concept of "stereoblock".

5) Strictly speaking, the toluene residue and commercial samples are not perfectly isotactic, and may be included in the concept of "stereoblock" generally. But the different behavior of motional narrowing, and crystallization from those of toluene and n-heptane extracts may enable us to call the toluene residue and commercial samples to be so-called "isotactic polymer"

6) The size of crystallites is slightly smaller in the quenched sample than in the annealed one.

7) The larger value of the rigid state second moment suggests the large contribution from the intramolecular interaction, which depends upon the position of methyl groups in the helical structure of the chain molecule.

Acknowledgement

The authors thanks are due to Professor S. Kambara and Mr. T. Oshika of Tokyo Institute of Technology for their courtesy of offering samples of atactic and stereoblock polymers, and to Mr. K. Abe for his helpful discussions and kind cooperation in this work, and for his permission of quoting his unpublished data. Further we are indebted to Mr. T. Uetake for his assistance in nuclear magnetic resonance experiment, Mr. K. Yanagisawa for his assistance in preparation of molded samples, and to Mr. T. Nagaoka for his assistance through the operation of extraction.

References

- 1) See for example, W. P. Slichter: *Fortschritte der Hochpolymerenforschung* (Springer, 1958) 35.
- 2) G. Natta: *J. Polymer Sci.* **16** (1955) 143.
- 3) W. P. Slichter and E. R. Mandel: *J. Chem. Phys.* **29** (1958) 232; *J. Appl. Phys.* **29** (1958) 1438.
- 4) J. A. Sauer, R. A. Wall, N. Fuschillo and A. E. Woodward: *J. Appl. Phys.* **29** (1958) 1385.
- 5) G. Natta et al.: *Gazetta Chim. ital.* **87** (1957) 528, 549, 570.
- 6) C. W. Wilson and G. E. Pake: *J. Polymer Sci.* **10** (1953) 503.
- 7) G. Natta et al.: *J. Polymer Sci.* **25** (1957) 119.
- 8) K. Abe and K. Yanagisawa: lecture at high polymer symposium (October, 1958, Osaka).
- 9) R. Nakane: unpublished.
- 10) K. Abe: to be submitted to *J. Polymer Science*.
- 11) N. Yamada and M. Tajima: *J. Appl. Phys. Japan* **27** (1958) 257 (in Japanese).
- 12) P. W. Anderson: *J. Phys. Soc. Japan* **9** (1954) 316.
- 13) R. Kubo and K. Tomita: *J. Phys. Soc. Japan* **9** (1954) 888.
- 14) G. Natta: *Materie Plastiche* **23** (1957) 541.
- 15) J. G. Powles: *Proc. Phys. Soc. London B*, **69** (1956) 281.
- 16) G. E. Pake: *J. Chem. Phys.* **16** (1948) 327.
- 17) E. R. Andrew and R. Bersohn: *J. Chem. Phys.* **18** (1950) 159.
- 18) H. S. Gutowsky, G. B. Kistiakowsky, G. E. Pake and E. M. Purcell: *J. Chem. Phys.* **17** (1949) 972.
- 19) B. D. Coleman: *J. Polymer Sci.* **31** (1958) 155.

On the Paramagnetic Inelastic Scattering of Neutrons due to Ions in the Anisotropic Crystalline Field

By Yasusada YAMADA

Department of Physics, Faculty of Science, Osaka University

(Received September 19, 1959)

The paramagnetic inelastic scattering of neutrons due to ions of 3d transition elements in the anisotropic crystalline field was considered. When the orbital momentum of the paramagnetic ions is not quenched, the spin states are no longer degenerate but split into discrete levels. The transition between these levels can occur by magnetic dipole interaction of ions with neutrons, neutrons losing or gaining the corresponding energy. In the special case of FeCl_2 , an antiferromagnetic crystal whose Néel temperature is 24°K , the calculation of the forward scattering cross-sections of neutrons in various temperatures and wave lengths were carried out which showed that it is possible, in the ordinary conditions, to observe the inelastically scattered neutrons, and whence to obtain an information about the energy level scheme of the atomic spin in the crystal.

§ 1. Introduction

In 1935, Van Vleck¹⁾ pointed out that neutrons would be scattered inelastically by a paramagnetic ion which has an exchange interaction with neighbouring magnetic ions. However, there should be another kind of inelastic paramagnetic scattering which occurs when neutrons interact with the spin magnetic moment of an iron group ion under the influence of a crystalline electric field. In this case neutrons will cause a transition of the spin state, losing or gaining an amount of energy corresponding to the energy difference between the spin levels. Thus it may be possible to obtain informations about the magnetic anisotropy of the crystal by analysing the energy change of the scattered neutrons. In the case of the inelastic scattering associated with the exchange interaction, the wave length of the scattered neutrons distributes themselves continuously around the incident wave length, in a manner which depends on the spread of the energy level of the atomic spin. In the case of the inelastic scattering associated with the magnetic anisotropy, however, the wave length distribution will be discrete, since the spin level splitting by the crystalline field is discrete.

When the orbital angular momentum is quenched, the spin level splitting of the magnetic ion under the influence of the crystalline field is rather small, being of the order

of 10 cm^{-1} or less. In such a case, the distribution of the scattered wave length will be overlapped by the continuous distribution, the width of which is in general larger than 10 cm^{-1} . When the orbital momentum is not quenched as in the case of FeCl_2 , which is an anti-ferromagnetic crystal whose Néel point is at 24°K , the spin level splitting appears to be of the order of 100 cm^{-1} . For the same case, the width of the energy spread of the neutron inelastically scattered by the exchange interaction is estimated to be about 15 cm^{-1} for the paramagnetic temperature region. Accordingly, it is expected that one should be able to observe a discrete wave length distribution of the scattered neutron wave. The purpose of the present paper is to investigate such a paramagnetic scattering for this particular case of FeCl_2 .

The Fe^{++} ion is in ^6D state when it is free. Its fivefold orbital degeneracy is not completely lifted by the cubic and trigonal crystalline field, and the ground state in this field is considered to be a doublet. The spin moment therefore feels a strong magnetic field through LS coupling, so that the spin levels belonging to the orbital ground state split into five levels each of which is doubly degenerate. The energy difference between neighbouring doublets is of the order of 100 cm^{-1} . A schematic diagram proposed by Kanamori²⁾ for the energy splitting of the spin states belonging to the orbital ground state is shown in

Fig. 1. The energy difference between the neighbouring spin levels, Δ , is the same for the five levels as long as the LS interaction is small compared with the orbital level splitting due to the crystalline field. Transition between these spin states due to the dipolar interaction between neutrons and atomic spin is possible only between neighbouring levels as will be proved later, so that the energy change of the inelastically scattered neutrons are confined to $\pm\Delta$. So, if the corresponding cross-section is large enough to allow for the observation, it should be possible to determine the level splitting Δ , or the coefficient of the LS coupling. In the following sections we shall calculate this cross-section.

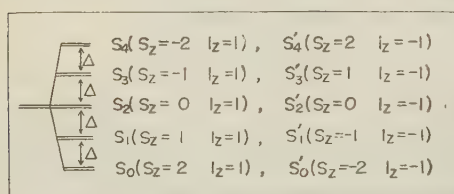


Fig. 1. The level scheme of orbital ground state of Fe^{++} ion in FeCl_2 crystal. S_z and L_z are the quantum numbers of z component of spin and orbital moment.

§ 2. Mathematical Details of Calculating the Inelastic Scattering Cross-Section

The amplitude of the neutron wave scattered by a paramagnetic ion, according to Halpern and Johnson³⁾ is given by,

$$\left(\frac{M_0}{\hbar k_0}\right)^{1/2} \left(\frac{e^2 g}{mc^2}\right) \cdot \sum_{s's'} \frac{e^{ik'r}}{r} (s', A' | s_n \cdot \mathbf{R} | s, A) \chi_s \psi_{A'},$$

where

$$\mathbf{R} = (\mathbf{e} \cdot \mathbf{P}_s) \mathbf{e} - \mathbf{P}_s + \mathbf{e} \times \left(\frac{\mathbf{P}_L}{\kappa} \right),$$

$$\mathbf{P}_s = \sum_i \mathbf{s}_i e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i}, \quad \mathbf{P}_L = \sum_i \left(\frac{i}{\hbar} \mathbf{p}_i \right) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i},$$

$$\mathbf{e} = \mathbf{k} - \mathbf{k}' / |\mathbf{k} - \mathbf{k}'|, \quad \kappa = |\mathbf{k}'|,$$

$\mathbf{s}_i$ and $\mathbf{p}_i$ are the spin moment and momentum of the i 'th electron, the summation over i extends over all the electrons in the ion; $\mathbf{k}$ and $\mathbf{k}'$ are the wave vectors of the neutron before and after scattering; χ_s is the wave function of the neutron spin s_n in state s ; ψ_A represents the wave function of the magnetic ion in state A ; g is the nuclear magneton

number, M_0 the mass of neutron, and k_0 the Boltzmann constant.

The differential cross section for unpolarized incident neutron beam when the paramagnetic ion is in thermal equilibrium is:

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2 g}{mc^2} \right)^2 \frac{\sum_{A,A'} e^{-E_A/k_0 T} \langle \mathbf{R}_{A'A} |^2}{\sum_A e^{-E_A/k_0 T}}, \quad (2)$$

where $\mathbf{R}_{A'A}$ denotes the matrix element of operator $\mathbf{R}$ and E_A is the energy of state A . When we are concerned with FeCl_2 in the temperature range of 50 °K–300 °K, it is allowed to extend the summation $\sum_{A'A}$ only over the spin states which belong to the orbital ground state because their overall separation is about 600 °K. The wave functions of the orbital ground state,²⁾ which are doubly degenerate, are

$$\left. \begin{aligned} \Phi_{a_1} &= \cos \alpha \psi_{-2} + \sin \alpha \psi_1 \\ \Phi_{a_2} &= \cos \alpha \psi_2 - \sin \alpha \psi_{-1} \end{aligned} \right\} \quad (3)$$

where α is a parameter which is determined by the ratio of the cubic to trigonal crystalline field acting on the magnetic ion ($\cos \alpha = \sqrt{2/3}$ when the trigonal field is zero). ψ_M represents the Slater wave function for the four electrons with $L_z = M$ belonging to the ${}^6D$ state, the direction of z being along the axis of three fold symmetry of the crystal. For example, ψ_2 is given explicitly by

$$\psi_2 = \frac{1}{\sqrt{4!}} \sum_P (-1)^P \mathbf{P} \{ \phi_2(1) \phi_1(2) \phi_0(3) \phi_{-1}(4) \}, \quad (4)$$

where the subscript numeral in the parenthesis indicates which electron occupies each particular orbital, $\mathbf{P}$ is the permutation operator representing the operation to interchange the electrons. ϕ_m is given by

$$\phi_m = \zeta(r) Y_{2,m}(\theta, \varphi), \quad (5)$$

$\zeta(r)$ being the normalized 3d radial wave function, $Y_{2,m}$ the spherical harmonic of degree 2. The wave functions of states A and A' are constructed by combining these two orbital states Φ_{a_1} , Φ_{a_2} with spin functions whose eigenvalues are $S_z = 2, 1, 0, -1, -2$ as shown in Fig. 1.

In the calculation of

$$(A' | \mathbf{P}_s | A) = \sum_i \int \psi_{A'}^* \mathbf{s}_i \psi_A e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} d\mathbf{r},$$

and

$$(A' | \mathbf{P}_L | A) = \sum_i \int \psi_{A'}^* \mathbf{p}_i \psi_A e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} d\mathbf{r},$$

we expand the term $e^{i(k-k')r}$ in spherical harmonics as follows;

$$e^{i(k-k')r} = \sum_l 4\pi e^{il\pi} j_l(\kappa r) \cdot \sum_{m=0}^l \{Y_{l,m}(\theta, \varphi) \cdot Y_{l,m}(\theta_1, \varphi_1) + C.C.\}, \quad (6)$$

where $j_l(\kappa r)$ is the so-called spherical Bessel function of order l , i.e., $j_l(\kappa r) = \sqrt{\pi/2\kappa r} J_{(1/2)+l}$, and θ, φ and θ_1, φ_1 are the polar angles of the vectors r and $k-k'$, the polar axis being taken along the trigonal axis of the crystal. Then the integral $(A'|P_s|A)$ is expanded as a series each term of which is proportional to

$$(i)^l \int \phi_m^* \phi_m Y_{l,m} j_l(\kappa r) dr. \quad (7)$$

The integral $(A'|P_L|A)$ is also expanded as a series each term of which is proportional to

$$(i)^l \int \phi_m^* (\text{grad } \phi_m) Y_{l,m} j_l(\kappa r) dr. \quad (8)$$

A product of two 3d wave functions, $\phi_m^* \phi_m$, is expressible as a linear combination of spherical harmonics of even degree, and a product of a 3d wave function and its gradient, $\phi_m^* \text{grad } \phi_m$, as a linear combination of those of odd degree. Accordingly, the integral (7) vanishes unless l is even, while the integral (8) vanishes unless l is odd. Thus $(A'|P_s|A)$ takes on only real values and $(A'|P_L|A)$ takes on only imaginary values. Physically, this means that scattering due to spin magnetic moment and that due to orbital magnetic moment are incoherent with each other. We can therefore separate the differential cross-section as follows:

The elastic scattering cross-section by spin moment: $(d\sigma/d\Omega)_{el,S}$.

The inelastic scattering cross-section by spin moment: $(d\sigma/d\Omega)_{in,S}$.

The elastic scattering cross-section by orbital moment: $(d\sigma/d\Omega)_{el,L}$.

The inelastic scattering cross-section by orbital moment: $(d\sigma/d\Omega)_{in,L}$.

Then, the total cross-section is given by the sum of the above four terms, each term being expressed as

$$\left. \begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{el,S} &= \left(\frac{e^2 g}{mc^2} \right)^2 \frac{\sum_A e^{-B_A/k_0 T} |R_{SAA}|^2}{\sum_A e^{-B_A/k_0 T}}, \\ \left(\frac{d\sigma}{d\Omega} \right)_{in,S} &= \left(\frac{e^2 g}{mc^2} \right)^2 \frac{\sum_{AA'} e^{-B_A/k_0 T} k'/k |R_{SAA'}|^2}{\sum_A e^{-B_A/k_0 T}}, \end{aligned} \right\}$$

$$\left. \begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{el,S} &= \left(\frac{e^2 g}{mc^2} \right)^2 \frac{\sum_A e^{-B_A/k_0 T} |R_{LAA}|^2}{\sum_A e^{-B_A/k_0 T}}, \\ \left(\frac{d\sigma}{d\Omega} \right)_{in,L} &= \left(\frac{e^2 g}{mc^2} \right)^2 \frac{\sum_{AA'} e^{-B_A/k_0 T} k'/k |R_{LAA'}|^2}{\sum_A e^{-B_A/k_0 T}}, \\ R_s &= (e \cdot P_s) e - P_s, \\ R_L &= e \times \left(-\frac{P_L}{\kappa} \right). \end{aligned} \right\} \quad (9)$$

As we see in equation (9), the operator R_s contains the atomic spin operator s in linear form, whence the probability of transition between A and A' , due to the spin-spin interaction, has non-zero value only when either $S_z^f = S_z^i$ or $S_z^f = S_z^i \pm 1$ where S_z^i and S_z^f denote the spin quantum numbers of initial and final atomic state, respectively. From this it follows that the energy change of neutrons scattered by atomic spin is confined to zero and $\pm \Delta$.

For a powder sample, we average the above expressions over the directions of the crystal-lites; then a calculation shows that they are expressed in the form,

$$\left. \begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{el,S} &= \left(\frac{e^2 g}{mc^2} \right)^2 \tau_1(\Delta, T) G_1(\kappa), \\ \left(\frac{d\sigma}{d\Omega} \right)_{in,S} &= \left(\frac{e^2 g}{mc^2} \right)^2 \tau_2(\Delta, T, E_0) G_2(\kappa), \\ \left(\frac{d\sigma}{d\Omega} \right)_{el,L} &= \left(\frac{e^2 g}{mc^2} \right)^2 \tau_1' G_1'(\kappa), \\ \left(\frac{d\sigma}{d\Omega} \right)_{in,L} &= \left(\frac{e^2 g}{mc^2} \right)^2 \tau_2'(\Delta, T, E_0) G_2'(\kappa). \end{aligned} \right\} \quad (10)$$

G_l and G_l' ($l=1, 2$) play the role of the form factor and vary with κ (the difference between the incident and scattered wave vectors) and are given explicitly by

$$G_l = \sum_{ij} c_i^l c_j^l J_i J_j, \quad i, j = 0, 2, 4$$

$$G_l' = \sum_{ij} c_i^l c_j^l J_i' J_j', \quad i, j = 1, 3$$

$$J_i = \int \xi^*(r) \xi(r) j_i(\kappa r) r^2 dr, \quad J_i' = \int \frac{\xi^* \xi}{\kappa r} j_i(\kappa r) r^2 dr, \quad (11)$$

where $\xi(r)$ is the radial 3d wave function, j_i is the spherical Bessel function of order i , c_i and c_j are certain numerical factors determined by the wave functions (3). As for the value of $\xi(r)$, we make use of the calculations for Co^{++} by Nagamiya and Motizuki⁽⁵⁾ using the Hartree wave function.

τ_i and τ_i' are related to the thermal distribution of the initial state, and moreover, in the case of inelastic scattering, to the initial neutron energy and the energy change due to scattering. They are given by

$$\left. \begin{aligned} \tau_1(\Delta, T) &= \frac{1 - e^{-\Delta/k_0 T}}{1 - e^{-5\Delta/k_0 T}} (4 + e^{-\Delta/k_0 T} + e^{-3\Delta/k_0 T} + 4e^{-4\Delta/k_0 T}), \\ \tau_2(\Delta, T, E_0) &= \frac{1 - e^{-\Delta/k_0 T}}{1 - e^{-5\Delta/k_0 T}} \left\{ \sqrt{1 + \frac{\Delta}{E_0}} \left(e^{-\Delta/k_0 T} + \frac{3}{2} e^{-2\Delta/k_0 T} + \frac{3}{2} e^{-3\Delta/k_0 T} + e^{-4\Delta/k_0 T} \right) \right. \\ &\quad \left. + \sqrt{1 - \frac{\Delta}{E_0}} \left(1 + \frac{3}{2} e^{-\Delta/k_0 T} + \frac{3}{2} e^{-2\Delta/k_0 T} + e^{-3\Delta/k_0 T} \right) \right\}, \\ \tau_1' &= 1, \\ \tau_2'(\Delta, T, E_0) &= \frac{1 - e^{-\Delta/k_0 T}}{1 + e^{-5\Delta/k_0 T}} \left\{ \sqrt{1 - \frac{4\Delta}{E_0}} + e^{-\Delta/k_0 T} \sqrt{1 - \frac{2\Delta}{E_0}} + e^{-3\Delta/k_0 T} \sqrt{1 + \frac{2\Delta}{E_0}} \right. \\ &\quad \left. + e^{-4\Delta/k_0 T} \sqrt{1 + \frac{4\Delta}{E_0}} \right\}, \end{aligned} \right\} \quad (12)$$

where $E_0 = (\hbar^2 k^2)/(2M_0)$ is the energy of the initial neutron wave, and Δ is the energy difference between neighbouring spin states. The terms multiplied by $\sqrt{1 - (\Delta/E_0)}$ represent the cross-sections for the inelastic scattering in which the atomic spin state is excited. Thus, if the incident neutron energy is not sufficient to excite the spin state, i.e., $\Delta \geq E_0$, these terms should vanish. The terms multiplied by $\sqrt{1 + (\Delta/E_0)}$ represent those for the de-excitation of the atomic spin state. Further, the terms multiplied by $\sqrt{1 \pm (2\Delta/E_0)}$, $\sqrt{1 \pm (4\Delta/E_0)}$ corresponds to the transitions between the two states whose energy changes are 2Δ and 4Δ . These transitions can occur only in the inelastic scattering due to the interaction between neutron spin and atomic orbital moment. Through this kind of scattering the orbital state of atoms changes, while the spin state must be the same before and after transition, or $S_z^f = S_z^i$. So that, as can be seen in Fig. (1), all allowed transitions are as follows:

$$\begin{aligned} S_0(S_z=2 \quad l_z=1) &\leftrightarrow S_4'(S_z=2 \quad l_z=-1) \\ S_4(S_z=-2 \quad l_z=1) &\leftrightarrow S_0'(S_z=-2 \quad l_z=-1) \\ &\text{1st kind} \\ S_1(S_z=1 \quad l_z=1) &\leftrightarrow S_3'(S_z=1 \quad l_z=-1) \\ S_3(S_z=-1 \quad l_z=1) &\leftrightarrow S_1'(S_z=-1 \quad l_z=-1) \\ &\text{2nd kind} \\ S_2(S_z=0 \quad l_z=1) &\leftrightarrow S_2'(S_z=0 \quad l_z=-1) \quad \text{3rd kind} \end{aligned}$$

The energy change in the first kind transition is 4Δ , that in second kind 2Δ , and in the third kind of transition the energy change is zero which is no more inelastic.

Therefore $(d\sigma/d\Omega)_{in,L}$ gives the scattered

neutron whose energy change is twice or four times as much as the scattering due to atomic spin. But the cross-section for these scatterings is quite small as compared with $(d\sigma/d\Omega)_{in,S}$ because the form factors for these scatterings are different. The main parts of the form factors for these scatterings are different. The main parts of the form factors are $(J_0)^2$ and $(J_1)^2$ in Eqs. (11) for $(d\sigma/d\Omega)_S$ and $(d\sigma/d\Omega)_L$ respectively. For the forward scattering, or for small κ , we can estimate the above value as follows:

$$\left. \begin{aligned} \lim_{\kappa \rightarrow 0} \left(\int \zeta^* \zeta j_0(\kappa r) r^2 dr \right)^2 &= \left(\int \zeta^* \zeta r^2 dr \right)^2, \\ \lim_{\kappa \rightarrow 0} \left(\int \frac{\zeta^* \zeta}{\kappa r} j_1(\kappa r) r^2 dr \right)^2 &\simeq \left(\int \frac{\zeta^* \zeta}{\kappa r} \cdot \frac{\kappa r}{3} r^2 dr \right)^2. \end{aligned} \right\} \quad (13)$$

So that $(d\sigma/d\Omega)_L$ is about 10% of $(d\sigma/d\Omega)_S$.

§ 3. Temperature and Wave Length Dependence of the Forward Scattering Cross-sections.

In Fig. 2 — Fig. 5 the calculated forward scattering cross-sections are shown, where we used the value 150°K for Δ and neglected the influence of the trigonal field on α , i.e., $\cos \alpha$ was assumed to be $\sqrt{2/3}$, which is enough for our present purpose to know the order of magnitude of the cross-sections and general features of their dependence on temperature and incident neutron wave length λ .

In Fig. 2 we see that $(d\sigma/d\Omega)_{el,S}$ decreases as the temperature is raised. This comes about because the scattering by the spin in the lowest level is the largest. It is not af-

ected by a change of λ , because κ for elastic forward scattering is always zero, and therefore the form factor is independent of λ . In the same figure it is seen however that

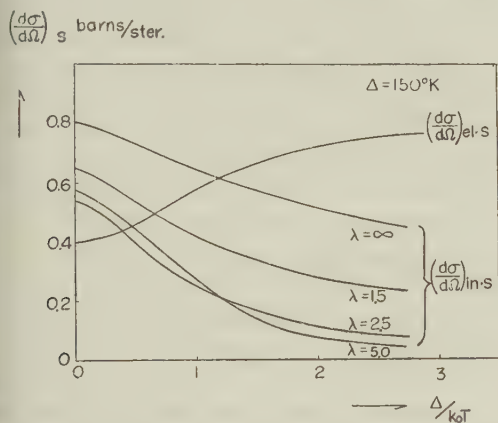


Fig. 2. Temperature dependence of forward scattering cross-sections, $(d\sigma/d\Omega)_{el,s}$ and $(d\sigma/d\Omega)_{in,s}$.

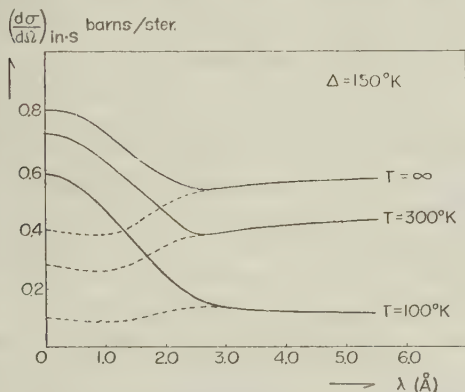


Fig. 3. Wave length dependence of forward scattering cross-section, $d\sigma/d\Omega)_{in,s}$, the part under the dotted line corresponds to the cross-section due to de-excitation of atomic spin state.

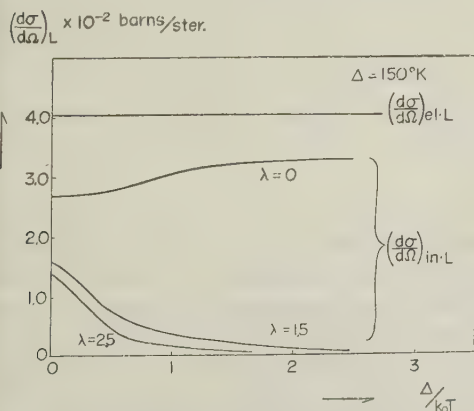


Fig. 4. Temperature dependence of forward scattering cross-sections, $(d\sigma/d\Omega)_{el,L}$ and $(d\sigma/d\Omega)_{in,L}$.

$(d\sigma/d\Omega)_{in,s}$ increase as the temperature is raised, as the spin in the upper states gives rise to larger cross-sections. As for dependence on λ , it is seen that the cross-section increases largely on the short wave length region. One of the reasons for this is that, for $\lambda < \sqrt{\hbar^2/2M_0\Delta}$, inelastic scattering in which neutrons lose energy can occur beside that in which neutron gain energy. Moreover,

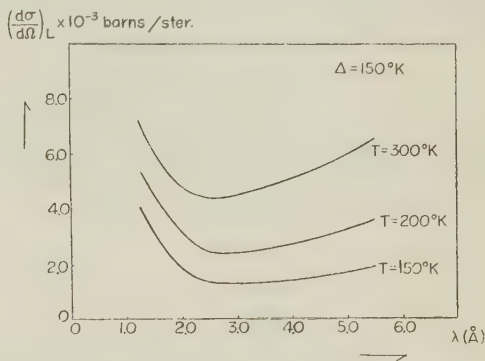


Fig. 5. Wave length dependence of forward scattering cross-section, $(d\sigma/d\Omega)_{in,L}$.

even for the forward scattering κ is not zero, but varies with λ , which makes the feature of the λ dependence rather complicated. In the limit of $\lambda \rightarrow 0$ ($\kappa \rightarrow \infty$), the relative energy change becomes zero, and inelastic scattering becomes substantially elastic scattering. Accordingly, in the limit of $T \rightarrow \infty$ and $\lambda \rightarrow 0$, there should be no effect of spin level splitting on the neutron cross-section, which predicts that in this limit, the sum of $(d\sigma/d\Omega)_{el,s}$ and $(d\sigma/d\Omega)_{in,s}$ should be equal to the spin paramagnetic cross-section given by Halpern and Johnson³⁾. In fact, we can see that

$$\lim_{\substack{T \rightarrow \infty \\ \lambda \rightarrow 0}} \left[\left(\frac{d\sigma}{d\Omega} \right)_{el,s} + \left(\frac{d\sigma}{d\Omega} \right)_{in,s} \right] = 4 \left(\frac{e^2 g}{mc^2} \right)^2 = \left(\frac{d\sigma}{d\Omega} \right)_{para} \quad (14)$$

$(d\sigma/d\Omega)_{el,L}$ shows neither wave length dependence as is the case of $(d\sigma/d\Omega)_{el,s}$, nor temperature dependence because in this scattering the orbital motion is common to all the levels. $(d\sigma/d\Omega)_{in,L}$ shows nearly the same temperature and wave length dependences as $(d\sigma/d\Omega)_{in,s}$ does, only its absolute value being much smaller than the scattering by the spin moment.

§ 4. Discussion

It was first predicted by Van Vleck¹⁾ that the exchange interaction between neighbouring paramagnetic spins would cause an inelastic scattering of neutrons, and in 1953, Brockhouse²⁾ observed the effect experimentally.

According to the theory of Van Vleck, this kind of inelastic scattering produces the wave length distribution for the scattered neutrons which is Gaussian in shape, the second moment of this distribution being given by

$$h\nu_{rms} = k_0[6\Theta^2/zS(S+1)]^{1/2}, \quad (15)$$

where Θ is the Curie-Weiss constant, z the number of nearest neighbouring spins, S the spin quantum number of the magnetic ion, k_0 the Boltzmann constant. For FeCl_2 ,

$$\Theta = 48^\circ\text{K},$$

$$S = 2,$$

$$z = 6.$$

Here we take as the value of z only the intralayer spins into account because the interlayer exchange interaction is much smaller than the intralayer interaction. From these values we obtain $h\nu_{rms}/k_0 \simeq 20^\circ\text{K}$. This width of energy distribution is quite small as compared with the discrete energy change of about 150°K (100 cm^{-1}).

The theory of the width of energy distribution was improved by De-Gennes³⁾. According to his theory, the second moment of the Gaussian distribution as defined above will depends on κ . For $\kappa=0$, the width is zero; as κ increases, the width tends to increase till it reaches a limiting value for $\kappa=\infty$, which is just the same value as that predicted by Van Vleck. Thus, in our case, where we are considering the forward scattering only, the second moment may be even smaller than the value given in Eq. (10).

To determine experimentally the crystal level splitting by the method given above, either the usual slow chopper or three crystal analysis of the inelastically scattered neutron may be used. In the specific case of FeCl_2 the sizable capture cross-section of the chlorine atoms may present some intensity problems. We have calculated the expected intensity for a sample thickness of $1/\mu$ which is around 0.6 cm for $\lambda=5\text{\AA}$, μ being the linear absorption coefficient.

The forward scattering intensity of inelastic

scattering is given by

$$I = I_0 \rho s d e^{-\mu d} \left(\frac{d\sigma}{d\Omega} \right)_{in} d\Omega, \quad (16)$$

where I_0 is the intensity of the incident neutron wave, ρ the density of the magnetic ions, d the thickness of the sample and s the area irradiated. Using the parameters given by

$$s = 10\text{ cm}^2,$$

$$\rho = 1.48 \times 10^{22}\text{ cm}^{-3},$$

$$d = 0.6\text{ cm},$$

$$\mu = 1.5\text{ cm}^{-1},$$

$$d\Omega = 10^{-3}\text{ ster.},$$

$$\left(\frac{d\sigma}{d\Omega} \right)_{in} = 0.4\text{ barns/ster. } (\lambda = 5\text{\AA}),$$

$$T = 300^\circ\text{K},$$

we calculated the ratio I/I_0 , which is found to be 1.31×10^{-6} . This means that for an average beam intensity such as $I = 10^6\text{ c/sec}$ the forward intensity of inelastically scattered neutrons comes out to be about 720 c/min. , which should be observable.

In the special case that the kinetic energy of incident neutron is almost equal to the energy of excitation of atomic state, the plane wave approximation for the inelastically scattered wave is no longer valid, that is, Born's approximation can not be used. In such a case, we must proceed as follows. As the interaction energy is much smaller than the energy separation of atomic state, the wave function of the total system for the inelastic scattering process may be given in the following form:

$$\Psi = (\text{atomic wave function in the excited state}) \times (\text{neutron wave function}),$$

where the neutron wave function is one of the function which satisfy the following Schrödinger wave equation,

$$\left. \begin{aligned} & \left[\frac{\hbar^2}{2M_0} \nabla^2 + \langle V \rangle \right] \psi_{\text{neutron}} = E \psi_{\text{neutron}}, \\ & \langle V \rangle = \int \psi_{\text{atom}}^* V \psi_{\text{atom}} d\tau_a, \end{aligned} \right\} \quad (17)$$

where V stands for the dipole-dipole interaction and Fermi interaction between atoms and neutrons, ψ_{atom} represents the atomic wave function in the excited state, $d\tau_a$ being the volume element of atomic coordinates. This potential energy is of the order of 10^{-3} cm^{-1} which means that the plane wave approximation is not valid only when $(2\pi^2 \hbar^2 / M_0)(1/\lambda^2)$

$-1/\lambda_0^2) \approx 10^{-3} \text{ cm}^{-1}$, where λ_0 corresponds to the wave length of exact resonance, $2\pi^2\hbar^2/M_0 \cdot 1/\lambda_0^2 = \Delta$. It follows therefore that this kind of anomaly occurs only in the wave length range of $10^{-5} \lambda_0$ around λ_0 . Moreover, the inelastic scattering cross-section, which contain the term k'/k , will tend to zero in the limit of $\lambda \rightarrow \lambda_0$ even if the transition probability suffers a finite modification. Thus, we expect no observable anomaly in the inelastic scattering. If there are trapped neutron states, which have discrete energy levels, as solutions of equation (17), resonance elastic scattering may occur which can be described analogously to the resonance nuclear scattering. If such occurs, it may be possible to observe an increase in elastic scattering around λ_0 .

Acknowledgements

The author wishes to express his cordial thanks to Prof. T. Nagamiya for his kind guidance. He is also indebted to Dr. K. Motizuki and Dr. M. Tatiki of Osaka University for their illuminating discussions throughout this work.

References

- 1) J. H. Van Vleck: *Phys. Rev.* **55** (1939) 924.
- 2) J. Kanamori: *Progr. Theor. Phys.* **20** (1958) 890.
- 3) O. Halpern and M. H. Johnson: *Phys. Rev.* **55** (1939) 898.
- 4) T. Nagamiya and K. Motizuki: *Rev. Mod. Phys.* **30** (1958) 89.
- 5) B. N. Brockhouse: *Phys. Rev.* **99** (1955) 601.
- 6) P. G. De-Gennes: *J. Phys. Chem. Solids* **4** (1958) 223.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 3, MARCH, 1960

Paramagnetic Resonance of Manganese in Alkali-Chlorides

By Hisamitsu YOSHIMURA*

Department of Physics, Faculty of Science, Kyoto University

(Received July 27, 1959)

The solution energies of manganese in LiCl and KCl crystals have been calculated by applying Haven's method to the systems of MnCl_2 -Alkali Chloride and by the use of the experimental value of the solution energy of manganese in NaCl, obtaining 0.85 eV for LiCl and -2.08 eV for KCl. The paramagnetic resonance spectra of manganese in quenched crystals of LiCl and KCl showed the hyperfine structure of divalent manganese ion in the crystalline field with non-cubic symmetry. By assuming the spin Hamiltonian of orthorhombic symmetry for the divalent manganese ion associated with a positive ion vacancy, the values of D and E have been calculated as $D=109 \pm 10$ gauss and $E=25 \pm 10$ gauss for LiCl. For KCl the observed spectra and their transformations by thermal treatments will be shown. The coloration of Mn doped crystals was carried out by γ -ray irradiation or by pointed cathode, and the resonance spectra of the colored crystals were observed.

§ 1. Introduction

It has been well known that the paramagnetic resonance of manganese in alkali-halides shows various spectra under thermal treatments. Oshima, Abe, Nagano and Nagusa¹⁾ pointed out, for the first time, the difference

of resonance spectra of some transition metals between quenched and slowly cooled alkali-chloride crystals. Schneider and Caffyn²⁾ found out independently that manganese in NaCl showed a complex spectrum composed of many hyperfine lines in quenched crystals and a broad line with the width of 400 gauss in slowly cooled crystals. They proposed some models for the states of manganese in

* Present address: Department of Physics, College of Science and Engineering, Nihon University, Tokyo.

the crystals, corresponding to the observed spectra. Watkins and Walker, and Morigaki, Fujimoto and Itoh³⁾ (hereafter referred to as M.F.I.) investigated this complex spectrum and successfully carried out analysis of it by assuming manganese ion associated with a metal ion vacancy. Further, Watkins⁴⁾ and Yokozawa⁵⁾ observed the transformations of resonance spectrum with increasing temperature and found the hyperfine structure of six lines caused by manganese in crystalline field with cubic symmetry. From these results they verified that the complex spectrum in quenched crystals resulted from the frozen state of manganese at high temperature. Fukuda, Uchida and the present author⁶⁾, and also Watkins⁷⁾ pointed out that these behaviors of manganese had the generality in other alkali-chloride crystals. Forrester and Shneider⁸⁾ extended the resonance experiments to KCl-Mn crystals from solution, and Fukuda, Uchida and the author⁹⁾ observed the hyperfine spectra of LiCl- and KCl-Mn crystals from the melt. Nowadays, it is understood that various paramagnetic resonance spectra of Mn in thermally treated alkali-halide crystals transform to each other and that the complex spectra in quenched crystals are due to divalent manganese ion in the orthorhombic crystalline field caused by a metal ion vacancy in its neighboring site.

In this paper will be first described the calculations of solution energy of manganese and its observed resonance spectra in LiCl-Mn and KCl-Mn single crystals from the melt, which were partly reported by us in the previous paper⁶⁾. Then the analysis of hyperfine structure will be shown for these crystals, especially in detail for LiCl-Mn, by using the model of Mn^{2+} ion associated with a positive ion vacancy. Further, the phenomena of coloration induced in LiCl-Mn, NaCl-Mn and KCl-Mn crystals by pointed cathode method or by γ -ray irradiation will be discussed in relation to the behaviors of resonance of

manganese in the colored crystals.

§ 2. Experimental Technique

The measurements of the electron spin resonance were carried out by a usual field modulation (30 c/sec) spectrometer, working at 24,000 Mc/sec. The power generator of klystron (2K33) was frequency-stabilized by using the circuits designed by Silsbee⁹⁾. Fig. 1 shows the block diagram of the spectrometer; the frequency modulation of klystron is performed at 455 Kc/sec, and the error signal of microwave frequency is detected as the deviation from a resonance frequency of the wave-meter ($Q=25,000$) used as a frequency reference. When the amplitude of modulation voltage E_m on the klystron repeller is small, the voltage of the microwave signal may be expressed by

$$E_0 \sin(\omega t + (K_f E_m / \omega_m) \sin \omega_m t),$$

where K_f indicates the change of microwave frequency per the change of unit repeller voltage, ω_m is frequency of modulating voltage E_m and ω microwave frequency. The above expression shows that the microwave signal from klystron is frequency-modulated. Then the output error signal from the reference wave-meter is proportional to the following expression because of the square-law detection of diode crystal;

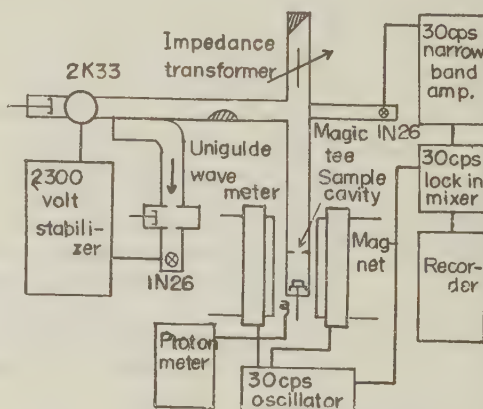


Fig. 1. Block diagram of spectrometer.

$$E_0^2 \frac{2}{Q^2} J_0(\delta_1) J_1(\delta_1) \left(\frac{\omega_m}{\omega_0} \right) \left(\frac{\omega_0 - \omega}{\omega_0} \right) \frac{1}{C} \sin \omega_m t$$

with

$$C = \left[\left(\frac{\omega_0 - \omega}{\omega_0} \right)^2 + \frac{1}{4Q^2} \right] \sqrt{\left[\left(\frac{\omega_0 - \omega - \omega_m}{\omega_0} \right)^2 + \frac{1}{4Q^2} \right] \left[\left(\frac{\omega_0 - \omega + \omega_m}{\omega_0} \right)^2 + \frac{1}{4Q^2} \right]}.$$

where Q is unloaded quality factor of reference cavity of resonance frequency ω_0 , Q_L its loaded quality factor, J_0 and J_1 are Bessel functions and $\delta_1 = K_f E_m / \omega_m$. In this expression the terms beyond second harmonics of ω_m are omitted. The above expression of error signal as a function of ω gives the dispersion curve with the center at a reference frequency of ω_0 . This error signal is negatively fed back to the klystron repeller through the phase detector and the frequency control is accomplished. For the klystron used K_f was 2.8 Mc/sec/volt and the modulating voltage was taken as $E_m = 0.02$ volt. The time constant of phase detector was set equal to $1/2\pi RC = 3$ c/sec from the considerations of Nyquist's condition and response speed for error signal. Thus the frequency control system worked in good conditions under the amplification of 60~80 db of error signal and the spectrometer showed the sensitivity of about 10^{15} spins gauss.

The cylindrical cavity of TE_{102} mode ($Q \approx 3,000$) was used as a sample cavity, and a sample of $0.5 \times 5 \times 5 \text{ mm}^3$ in dimension was set on the bottom of the cavity. The angle between the crystal axis and D.C. magnetic field was varied by a rotation around the vertical axis of the electromagnet.

§ 3. Solubility of Mn in Alkali Chlorides

It may be useful in experimental procedures to know how much manganese is soluble in alkali chloride crystals, and so the solution energies of Mn in these crystals were calculated for the MnCl_2 and alkali chloride systems. Haven¹⁰⁾ carried out the calculations of solution energy of Mg in LiCl crystal from the MgCl_2 and LiCl system. MnCl_2 has the same crystallographic structure as MgCl_2 , that is, CdCl_2 structure¹¹⁾, and its unit cell is shown in Fig. 2 together with the crystal constants, where d indicates the ionic distance for the

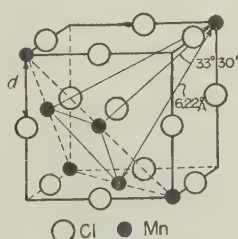


Fig. 2. The crystal structure of MnCl_2 .

ideal cubic arrangements of univalent chlorine ions obtained by slight deformation of MnCl_2 crystal.

The solution energy is defined by the difference between the sums of Madelung, polarization and repulsive energies for the two systems: Mn^{++} in MnCl_2 crystal and Mn^{++} plus one free positive ion vacancy in alkali halide crystal. Madelung energy is estimated from the expression $\alpha_M e^2/d$, where α_M is 2.1845 for MnCl_2 , 1.7476 for alkali chlorides and the values of lattice constants are given in the first row of Table I. The polarization

Table I.

Crystal	MnCl	LiCl	NaCl	KCl
Lattice constant	2.55Å	2.57Å	2.82Å	3.14Å
Madelung energy	24.6eV.	19.6eV.	17.9eV.	16.1eV.
Repulsive energy $n=9$	2.73eV.	2.54eV.	1.14eV.	0.41eV.
Polarization energy	1.66eV.	7.32eV.	7.22eV.	5.76eV.
Solution energy		+0.85eV.	+0.45eV.	-2.08eV.
Experimental value by Haven			+0.44eV.	

energy of Mn^{++} plus one positive ion vacancy in alkali chloride is calculated from the lattice energy and the formation energy of a pair of separated vacancies. The values of the latter are 2.12 eV, 2.02 eV and 2.25 eV for LiCl and KCl respectively, by taking the average of the values measured by Kelting, Witt, Wagner and Hantelman¹²⁾. The polarization energy for Mn^{++} vacancy in MnCl_2 can be estimated by making use of the above polarization energy of alkali chloride, as discussed by Haven. The repulsive energy is assumed to be proportional to $1/r^n$, but the value of n is not known for Mn^{++} in both MnCl_2 and alkali chlorides. Therefore, assuming that the n -value is the same for all the crystals now under consideration, it was determined in such a way that the calculated value of the solution energy of Mn in NaCl, which contains n as a parameter, becomes equal to its experimental value of 0.44 eV (in the temperature range of $200^\circ\text{C} \sim 400^\circ\text{C}$)¹³⁾.

Thus the value of n was determined as 9,* and then the solution energies of Mn in LiCl and KCl were calculated by using this n -value. The results of the calculations are shown in Table I. By the above method of calculation a considerable error may be introduced into the values of solution energy, but it seems likely that these values indicate the tendency of the change in Mn solubility for different solvent crystals. From the calculated value of solution energy it is considered that Mn is not soluble in KCl, but it is, in fact, soluble in KCl and the hyperfine structure of Mn is observed, which is most weak in its intensity and most unstable in comparison with that in NaCl or LiCl as described in the next section.

§ 4. Paramagnetic Resonance Spectra of LiCl-Mn and KCl-Mn

(1) Transformations of resonance spectra

Single crystals of LiCl-, NaCl- and KCl-Mn were grown by Kyropolous method from the melting phase containing 1 mol % manganese chloride. Since LiCl crystals are very hygroscopic, the crystal growth was performed as follows: when the temperature of the furnace gradually fell down to about 400°C after growing up of a single crystal by some volume, the grown crystal was brought out from the furnace and quenched to room temperature. Then the thermal treatment of crystal samples, slowly cooling or quenching, was carried out by holding them in a evacuated glass tube. For resonance experiments samples were coated with polyvinyl lacquer and set into the sample capity. Both the quenched and the slowly cooled LiCl-Mn crystals gave the same hyperfine spectrum of strong intensity, though the latter showed also a very weak line with the width of about 500 gauss, and the hyperfine spectrum did not bleach for a few months. Contrary to these behaviors, the slowly cooled NaCl-Mn crystals had only a broad line with the width of about 150 gauss; and the hyperfine lines, which appeared in the quenched crystals, bleached out after a few days, as observed also by M.F.I.³⁾

The grown crystal of KCl-Mn was separable

* The n -value of 8 given in the previous report⁶⁾ is incorrect, and hence the calculated values given there of solution energy are somewhat different from those in Table I.

in three parts, that is, transparent, cloudy and opaque parts with distinct boundaries. The paramagnetic resonance experiments were mainly carried out on the samples taken from the cloudy part. The transparent part showed too weak resonance pattern to carry out fine measurements. The opaque part had a line of the width of 20~50 gauss, which persisted and hardly transformed to other spectrum by any thermal treatment. In the slowly cooled crystal sample from the cloudy part the overlapping lines of about 100 gauss and about 30 gauss in width were observed. When this sample was quenched from 300~500°C after heating of short time period (about 30 minutes), only one line of about 30 gauss remained. By further quenching of this sample, the complex hyperfine spectrum was observed, only central six lines of which were found in the previous paper⁶⁾, but the period of heating necessary for the appearance of this complex spectrum seemed to depend on the local position in the cloudy crystal part. This complex spectrum, the intensity of which was much weaker than those of NaCl- and LiCl-Mn, bleached out within a period of 20 hours, and could not be reproduced by further quenching. From the complex behaviors of KCl-Mn resonance above described, it was difficult to standardize crystal samples and to obtain concrete informations of the transformations of spectra. Furthermore, the weak intensity of the hyperfine spectrum did not allow to analyze exactly its complex pattern, but it was found that the analysis of this pattern could not be performed only by the model of Mn^{++} associated with a metal ion vacancy in its nearest neighbor. The observed hyperfine spectrum is shown in Fig. 3 and from this spectrum the following values have been

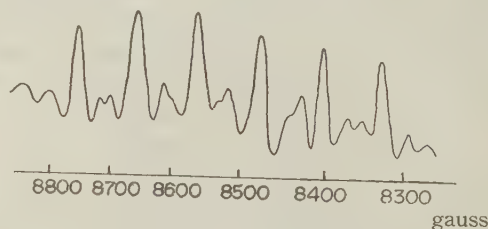


Fig. 3. a. The observed spectrum of LiCl-Mn in [100]. b. The schematic representation of the observed spectrum. c. The schematic representation of hyperfine lines for $\theta=45^\circ$ (abundance 4). d. The schematic representation of hyperfine lines for $\theta=90^\circ$ (abundance 2).

tentative derived; $g=2.005\pm0.002$ and $A=83\pm5$ gauss.

A number of investigators^{2),3),4)} suggested that the broad line spectra resulted from Mn^{++} in some coagulation state and their widths might be explained by the exchange narrowing caused by these Mn^{++} . The degrees of stability of the hyperfine pattern in each solvent crystal seems to show correspondence to the calculated values of solution energy in section 3, and this correspondence may be plausible, if the structure of the coagulation of Mn^{++} is similar to that of the $MnCl_2$ crystal shown in Fig. 2. Such a model of Mn^{++} arrangement with the same lattice constant as host crystal was examined by Oshima, Abe, Nagano and Nagusa¹⁾, and was considered unlikely because the line width of 30 gauss observed by them for NaCl-Mn fell too short of the value (360 gauss) expected from the exchange narrowing. It may be allowed, however, to consider that the coagulation state of Mn^{++} similar to this model gives the observed line width of about 150 gauss on account of the exchange narrowing.

(2) Analysis of hyperfine structure of LiCl-Mn

The observed hyperfine spectrum of LiCl-

Mn is very simple for the magnetic field H in [100] direction compared with those of NaCl-Mn and KCl-Mn, as shown in Fig. 4. Since it has direction-dependent lines other than six central hyperfine lines, following spin-Hamiltonian in the crystalline field of rhombic symmetry originated from an associated vacancy is used:

$$H = g\beta SH + DS_z^2 + E(S_x^2 - S_y^2) - \frac{1}{3}S(S+1) + ASI.$$

Here g , the spectroscopic factor, is assumed isotropic. β is the Bohr magneton, H the external field and S the electron spin operator. After the analysis of the spectrum of NaCl-Mn by M.F.I., the z -axis is taken as the direction connecting Mn^{++} site with the positive ion vacancy in its nearest neighbor.

When magnetic field H is in [100] direction of the crystal axis, equivalent vacancy sites are classified into two kinds on account of crystal symmetry, for which the angles between the magnetic field and the z -axis are 45° and 90° respectively. Using Eq. (3) and Table I in M.F.I., one obtains the following expressions for each transition representing the fine structure of spectrum.

(I) For $\theta=45^\circ$,

$$\begin{aligned} M=3/2 \rightarrow 5/2 & \quad H_1 = H_0 - (D+3E) - \frac{8(D-E)^2}{H_0} + \frac{(D+3E)^2}{4H_0}, \\ M=1/2 \rightarrow 3/2 & \quad H_2 = H_0 - \frac{(D+3E)}{2} + \frac{(D-E)^2}{H_0} + \frac{5(D+3E)^2}{16H_0}, \\ M=-1/2 \rightarrow 1/2 & \quad H_3 = H_0 + \frac{4(D-E)^2}{H_0} - \frac{(D+3E)^2}{2H_0}, \\ M=-3/2 \rightarrow -1/2 & \quad H_4 = H_0 + \frac{D+3E}{2} + \frac{(D-E)^2}{H_0} - \frac{5(D+3E)^2}{16H_0}, \\ M=-5/2 \rightarrow -3/2 & \quad H_5 = H_0 + (D+3E) - \frac{8(D-E)^2}{H_0} + \frac{(D+3E)^2}{4H_0}, \end{aligned}$$

(1)

(II) For $\theta=90^\circ$,

$$\begin{aligned} M=3/2 \rightarrow 5/2 & \quad H_1 = H_0 + 2(D+3E) + \frac{(D-E)^2}{H_0}, \\ M=1/2 \rightarrow 3/2 & \quad H_2 = H_0 + (D+3E) - \frac{5(D-E)^2}{H_0}, \\ M=-1/2 \rightarrow 1/2 & \quad H_3 = H_0 - \frac{2(D-E)^2}{H_0}, \\ M=-3/2 \rightarrow -1/2 & \quad H_4 = H_0 - (D+3E) - \frac{5(D-E)^2}{H_0}, \\ M=-5/2 \rightarrow -3/2 & \quad H_5 = H_0 - 2(D+3E) + \frac{(D-E)^2}{H_0}. \end{aligned}$$

If m is the magnetic quantum number of nuclear spin, for the transition $M \rightarrow M+1$ and $\Delta m=0$ the following terms must be added to the values of H in Eq. (1):

$$-Am - \frac{A^2}{2H_0} \{I(I+1) - m^2 + M(2M+1)\}. \quad (2)$$

For the magnetic field H in [110] the expressions of fine structure transitions must be classified into three kinds corresponding to

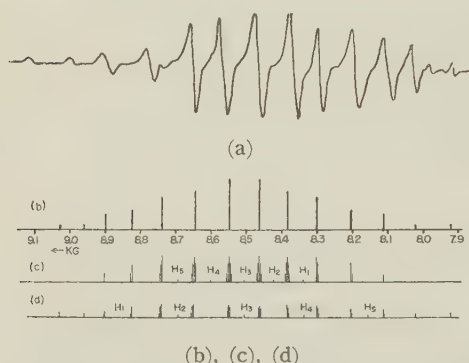


Fig. 4. a. The higher field part of the observed spectrum of LiCl-Mn in [100]. b. The schematic representation of the observed spectrum. c. The schematic representation of hyperfine lines for $\theta=0^\circ$ (abundance 1) derived from the observed spectrum.

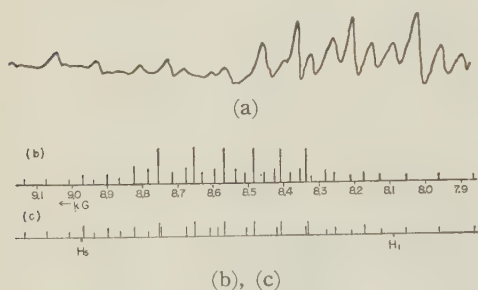


Fig. 5. A part of the observed spectrum of KCl-Mn in [100]. Here are shown the six hyperfine lines of transition $M=-1/2 \rightarrow 1/2$ and the spectra in the neighborhood of these lines.

$\theta=0^\circ, 60^\circ$ and 90° by taking account of the orientations of Mn^{++} plus a vacancy with respect to H , and so the observed spectrum is more complicated than that in [100] direction, as shown in Fig. 5-a.

From the expressions in Eq. (1),

$$H_1 - H_5 = 2(H_2 - H_4) \\ \text{for both } \theta=45^\circ \text{ and } 90^\circ,$$

and

$$H_2 - H_4 = -(D+3E) \text{ for } \theta=45^\circ, \\ = 2(D+3E) \text{ for } \theta=90^\circ. \quad (3)$$

From the hyperfine pattern in Fig. 4-a, the following results consistent with the above calculations can be easily derived, independently of whether the sign of $(D+3E)$ is positive or negative; $|H_1 - H_5| = 349$ gauss and $|H_2 - H_4| = 173$ gauss for $\theta=45^\circ$, $|H_1 - H_5| = 710$ gauss for $\theta=90^\circ$, and hence $|D+3E| = 173$ gauss. Here the positions of H_1 , H_2 , H_4 and H_5 in Fig. 4-b are shown for positive $D+3E$, but the order of arrangements of H must be reversed for negative $D+3E$. In order to determine the sign of $D+3E$, one uses the overall spacing of six hyperfine lines, $-5A - 5(A^2/2H_0)(2M-1)^{14}$, derived from Eq. (2). Here A may be assumed to be negative¹⁵. The transition $M=-5/2 \rightarrow -3/2$ in [110] fall in the high field side of H_0 for negative $D+3E$ and in the low field side for positive $D+3E$. On the other hand, the overall spacing of hyperfine lines of the transition $M=3/2 \rightarrow 5/2$ is smaller than that of $M=-5/2 \rightarrow -3/2$. Accordingly, the sign of $D+3E$ can be determined from Figs. 3-c and 4-b; in practice, it was confirmed by using both the pattern of 45° in [100] and that of 60° in [110], because the accuracy in the calibration of magnetic field was bad, that is, about ± 15 gauss, outside the range of magnetic field between 9000 gauss and 8000 gauss. Thus $D+3E$ was determined to be $+173$ gauss.

From the expressions representing the fine structure of resonance pattern in [110], the following expressions for $\theta=0^\circ$ can be derived:

$$M=3/2 \rightarrow 5/2 \quad H_1 = H_0 - 4D + 4E^2/H_0, \\ M=-5/2 \rightarrow -3/2 \quad H_5 = H_0 + 4D + 4E^2/H_0.$$

Therefore, the value of D can be determined from the resonance pattern of [110] in both extreme field sides. The sign of D can also be decided in a similar way to the above procedure, but it was impossible on account of inaccuracy in the calibration of higher or lower magnetic field. The absolute value of D was found to be 109 gauss.

For the determination of the values of D and E , the following quantity was introduced by taking the difference between H_3 's of $\theta=45^\circ$ and 90° in Eq. (1);

$$(D-E)^2 = (D+3E)^2/12 + \frac{1}{2}H_0\Delta H,$$

where $\Delta H = H_3(45^\circ) - H_3(90^\circ)$. ΔH gives the

degree of superposition of the hyperfine lines centered at H_3 for $\theta=45^\circ$ and those for $\theta=90^\circ$ in [100] direction and it may be less than the observed width of hyperfine line. Hence, by taking at most 15 gauss for ΔH , we obtained $|D-E| \leq 150$ gauss. By making use of this relation together with $D+3E=173$ and $D=109$ gauss, the following values were determined;*

$$\begin{aligned} g &= 2.003 \pm 0.001, \\ A &= 82 \pm 5 \text{ gauss}, \\ D &= 109 \pm 10 \text{ gauss}, \\ E &= 25 \pm 10 \text{ gauss}. \end{aligned}$$

§ 5. Coloration of Alkali Chloride-Mn Crystals

(1) Experiments on coloration

The coloration of alkali chloride-Mn crystals by Co^{60} γ -ray or by pointed cathode method was investigated. γ -ray irradiation of crystals was carried out at room temperature for about 100 hours (dosage: 2×10^6 röntgen/hour), and the coloration by pointed cathode was performed at the temperature of $500^\circ\text{C} \sim 600^\circ\text{C}$ by using a cathode of platinum wire and an anode of graphite plate. Optical absorptions of colored crystals were measured by Beckman DU spectrophotometer.

(i) Case of NaCl-Mn: Slowly cooled crystals showed the optical absorptions of F - and V_2 -centers after γ -ray irradiation, as shown in curve I of Fig. 6, and the ratio of the intensity of V_2 absorption to that of F absorption was larger than that in pure NaCl crystals. The resonance absorption of manganese with the width of 150 gauss seemed to be somewhat reduced by γ -ray irradiation.

Quenched crystals having the hyperfine spectrum of Mn^{++} associated with a vacancy were colored in dark brown by γ -ray irradiation, but they did not practically show the absorption of F and V_2 centers; the optical absorption curve is shown as curve II in Fig. 6. The effects of γ -ray irradiation on the resonance absorption were examined also on

quenched crystals by taking care of thermal bleaching of hyperfine pattern at room temperature. The quenched sample showing strong hyperfine spectrum was cut into two parts, and one part was irradiated by γ -ray, while the other part was not irradiated and used as a reference sample. After the period of 100 hours this reference sample showed the line of 150 gauss width and the hyperfine pattern, the latter being so weak that only six direction-independent lines were observed. On the other hand, the irradiated sample gave only the line of 150 gauss, the intensity of which was much smaller than that in the reference sample.

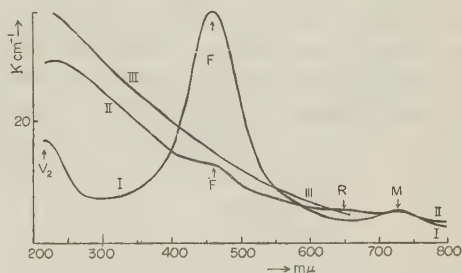


Fig. 6. The optical absorptions of NaCl-Mn colored by γ -ray irradiation and pointed cathode method. Curves I and II show the absorptions of slowly cooled and quenched crystal irradiated by γ -ray, respectively. Curve III is the absorption colored by pointed cathode method.

In the electrolytic coloration the boundary of the range colored in dark brown went towards the anode with the passage of time after the voltage was applied. This phenomenon was quite similar to F -coloration of pure NaCl crystals, but the darkening of the crystal was not due to F -absorption. The optical absorption of this crystal is nearly the same as that of the quenched crystal irradiated by γ -ray, as shown in curve III of Fig. 6. The darkening, which occurred more easily at higher temperature, did not disappear by flowing conversely the electric current with pointed anode or by any thermal treatment, though the colored crystal was heated up to the temperature right below the melting point. These behaviors are quite different from those of F -coloration in pure crystals.

Darkening by pointed cathode was stopped before the colored range reached the anode, and then electron spin resonance was measured in colored and uncolored parts. Though the

* If one takes the crystal axis as the z axis of spin Hamiltonian instead of the Mn^{++} -vacancy direction, as used by Watkins, D and E must be transformed according to $-(D+3E)/2$ ($\equiv D_0$) and $-(D-E)/2$ ($\equiv E_0$) respectively¹⁰⁾. Thus from the values of D and E , we obtained $D_0 = -86$ gauss and $E_0 = 44$ gauss. These values are in good agreement with those derived by Watkins.

same spectrum composed of a broad line of about 150 gauss width and weak six hyperfine lines was observed in each part as shown in Fig. 7, its intensity in the colored part was smaller by about 60% than that in the uncolored part. When both parts were quenched again from the temperature of about 600°C, a broad line disappeared and the hyperfine pattern was enhanced to show direction dependent lines. This is just like the behaviors of resonance spectrum in uncolored crystals. In this case the darkening of crystal was, of course, unchanged.

(ii) Case of KCl-Mn: The irradiation of γ -ray was carried out only for slowly cooled samples taken from both cloudy and opaque crystal parts. The coloration in both samples was due to F - and V_2 -absorptions (See Fig. 8), and these absorptions in the cloudy sample were more intense and stable than those in

the opaque one. F - and V_2 -centers in the opaque sample thermally bleached rather fast at room temperature, just like those in pure KCl crystals. The change of the resonance absorption in opaque samples was not recognized after γ -ray irradiation, but the line of 100 gauss width in cloudy samples was reduced by about two thirds in its intensity after irradiation.

The coloration of KCl-Mn by pointed cathode was performed for cloudy samples and its behaviors were different from those of NaCl-Mn. Fig. 8 shows the optical absorption of colored crystal; here F -absorption is dominant, but the absorption similar to that of NaCl-Mn colored by pointed cathode is seen in the ultraviolet region. In the resonance experiments no appreciable absorption was observed except that of F -center after coloration.

(iii) Case of LiCl-Mn: LiCl-Mn crystals, which have the hyperfine spectrum, gave F -absorption band (390 m μ) after γ -ray irradiation. The informations of absorption in shorter wavelength range below 300 m μ could not be obtained on account of the absorption of the polyvinyl film coating the crystal for optical measurements. The spin resonance spectrum of the colored crystal gave a broad line of about 500 gauss width in addition to the hyperfine pattern, the intensity of which was somewhat weaker than that before coloration.

(2) Discussions on coloration

From the above experiments it has become clear that the quenching of F -centers occurs in both the darkening by pointed cathode and that of quenched crystals by γ -ray irradiation for NaCl-Mn. As proved out by Watkins and Yokozawa^{4),5)} in resonance experiments, most of Mn^{++} ions are dispersed in the crystal from their coagulated states and many free positive ion vacancies are generated at such a high temperature as that of electrolytic coloration. Hence the electrons injected from pointed cathode will be captured by isolated Mn^{++} ions, if the probability of Mn^{++} for electron capture is larger than that of negative ion vacancy, and then Mn^{++} ion or its complex may be formed in the crystal instead of F -centers. This mechanism of F -center quenching may be supported to some extent by the following experimental results: the darkening by the absorption in the ultraviolet region

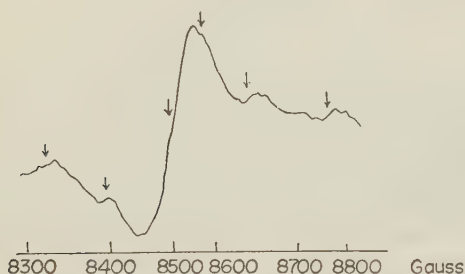


Fig. 7. The electron spin resonance spectrum of NaCl-Mn colored by pointed cathode method. Six arrows show the positions of the six hyperfine lines independent of direction. The broad line of about 150 gauss in width is considered to be the resonance absorption corresponding to coagulation state of Mn.

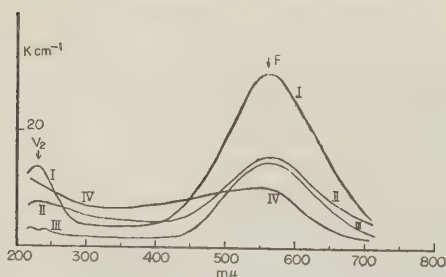


Fig. 8. The optical absorptions of KCl-Mn colored by γ -ray and pointed cathode method. Curves I, II and III show the absorptions of cloudy and opaque parts of KCl-Mn and pure KCl after γ -ray irradiation, respectively. Curve IV is the absorption colored by pointed cathode method.

(curve III in Fig. 6) and the reduction of the intensity of Mn^{++} resonance spectrum in the colored crystal. The darkening of quenched NaCl-Mn crystals by γ -ray will also be explained by using the above considerations. Mn^{++} ion and a positive ion vacancy are associated in the quenched crystal and they may be dissociated by thermal spike caused by γ -ray irradiation. Then isolated Mn^{++} ions and excess free positive ion vacancies will catch free electrons and holes created by γ -ray to form Mn^{+} - and V -type centers, respectively.* The darkened crystal, in fact, shows the same optical absorption as that of the electrolytically colored crystal and an absorption near 220 m μ in the ultraviolet region (curve II in Fig. 6). On the other hand, the hyperfine spectrum of Mn^{++} ion plus a positive ion vacancy completely vanished after γ -ray irradiation. From the above explanations there seems to be no resonance absorption attributed to Mn^{+} type center. Hayes and Jones¹⁷⁾ reported Llewellyn's resonance experiments of irradiated NaF-Mn, in which any spectrum attributed to Mn^{+} was not found even at 4°K.

In the pointed cathode experiments of KCl-Mn crystals the darkening was mainly due to F -absorption, and the absorption corresponding to that of the electrolytically colored NaCl-Mn was very weak (curve IV, Fig. 8). In the resonance experiments of the colored crystal no line was observed. In this case it may be considered that the quenching of F -center could not be clearly observed because of the following reasons; that is, the Mn content in KCl-Mn single crystal is very small on account of the low solubility of Mn and hence the number of free Mn^{++} ions become extremely small, particularly depending on the conditions of coloring operations. But further investigations will of course be necessary for definite conclusions.

In the γ -ray coloration of slowly cooled NaCl-Mn and KCl-Mn (cloudy) crystals the darkening was sensitized and the ratio of the number of V_2 -centers to that of F -centers was larger than the ratio of pure crystals. It is well known that the sensitization occurs in KCl-Ca crystals, in which positive ion vacan-

cies are not associated with Ca^{++} ions¹⁸⁾. On the other hand, from the ionic conductivity experiments⁹⁾, the conductivity of slowly cooled crystal of NaCl-Mn is lower than that of quenched one. Therefore, the above sensitization phenomenon seems to contradict to the conductivity experiments. But it may be allowed to consider tentatively that free excess positive ion vacancies are supplied by γ -ray irradiation from the coagulation states of Mn^{++} ions and they contribute to the sensitization of darkening. The resonance experiments did not give any information supporting the above consideration and so further experiments are necessary.

The above explanation of the F -center quenching may be contradictory to the γ -ray darkening of LiCl-Mn crystal, since Mn^{++} ions in LiCl are in dispersed state and F -coloration occurs. Moreover, this crystal was not colored by pointed cathode method. These problems are not yet solved.

§ 6. Summary

(1) It was found out that the state of Mn^{++} associated with a positive ion vacancy was most stable in LiCl at room temperature. It has been considered that the complex behaviors of KCl-Mn in thermal treatments, which depend on crystal samples, show the low solubility on Mn in KCl crystals. The results of the calculations of solution energy indicated the tendency of solubility corresponding to the above facts.

(2) The electron spin resonance of LiCl-Mn and KCl-Mn was observed, and the spectrum of LiCl-Mn was analyzed, assuming the model of Mn^{++} associated with a positive ion vacancy. The constants of spin Hamiltonian have been estimated for LiCl-Mn as follows: $g=2.003\pm0.001$, $A=82\pm5$ gauss, $D=109\pm10$ gauss and $E=25\pm10$ gauss. Though the spectrum of KCl-Mn was not analyzed, the values of g and A have been given from the direction independent hyperfine lines as follows: $g=2.005\pm0.003$ and $A=83\pm5$ gauss.

(3) The experiments of coloration of LiCl-, NaCl- and KCl-Mn were carried out by γ -ray irradiation and pointed cathode method. In the NaCl-Mn it was found that the quenching of F center occurred in colored crystals by pointed cathode and in quenched crystals irradiated by γ -ray. About these phenomena

* It would be unlikely from the experiments of Z -centers of alkali halide crystals containing divalent ions that a free electron is trapped by Mn^{++} associated with a positive ion vacancy.

some speculations have been performed.

Acknowledgements

The author wishes to express his sincere thanks to Prof. Y. Uchida and Dr. K. Fukuda of Kyoto University for their continual guidance and encouragements throughout this work, and to Dr. Y. Nakai for his kind interest and discussions. He further appreciates the valuable and kind assistance of Mr. H. Matumoto. He wish also to record his indebtedness to the Dr. H. Abe, who made a small quantity of the D.P.P.H. available to him. Finally, he would like to express his deep thanks to Dr. G. D. Watkins of General Electrics for kindly supplying his paper prior to publication.

References

- 1) K. Oshima, H. Abe, H. Nagano and M. Nagusa: J. Chem. Phys. **23** (1955) 1721.
- 2) E. E. Schneider and J. E. Caffyn: *Defects in Crystalline Solids* (The Physical Society, London, 1955) 74.
- 3) G. D. Watkins and R. M. Walker: Bull. Amer. Phys. Soc., II, **1** (1958) 135. K. Morigaki, M. Fujimoto and J. Itoh: J. Phys. Soc. Japan **13** (1958) 1174.
- 4) G. D. Watkins: Phys. Rev. **113** (1959) 79.
- 5) Y. Yokozawa and S. Ogawa: Presented at the annual meeting of the Physical Society of Japan, October 1958.
- 6) K. Fukuda, Y. Uchida and H. Yoshimura: J. Phys. Soc. Japan **13** (1958) 971.
- 7) *ibid.*
- 8) P. A. Forrester and E. E. Schneider: Proc. Phys. Soc. London **B**, **69** (1956) 833.
- 9) R. H. Silsbee: Technical Report No. 2211 (Harvard Univ., January 5, 1956) (unpublished).
- 10) Y. Haven: Rec. Trav. Chim. Pays-Bas **69** (1950) 1505.
- 11) *Struktur-Berichte I*, p. 158.
- 12) F. Seitz: Rev. Mod. Phys. **26** (1954) 13. Y. Haven: Rec. Trav. Chim. Pays-Bas **69** (1950) 1471. H. W. Etzel and R. J. Maurer: J. Chem. Phys. **18** (1950) 1003. H. Kelting and H. Witt: Z. Phys. **126** (1949) 607. C. Wagner and P. Hantelman: J. Chem. Phys. **18** (1950) 72.
- 13) Y. Haven: *Defects in Crystalline Solids* (The Physical Society, London, 1955) 261.
- 14) B. Bleany and D. J. E. Ingram: Proc. Roy. Soc. A, **201** (1959) 366.
- 15) W. Low: Phys. Rev. **105** (1957) 793.
- 16) K. D. Bowers and J. Owen: Rep. Progr. Phys. **18** (1955) 304.
- 17) W. Hayes and D. A. Jones: Proc. Phys. Soc. London **71** (1958) 503.
- 18) H. W. Etzel: Phys. Rev. **87** (1952) 906.
- 19) F. Seitz: Phys. Rev. **87** (1952).

On the Proton Resonance of Several Hexammine Complex Salts

By Pil Hyon KIM*

Department of Physics, Tokyo Metropolitan University, Tokyo

(Received August 11, 1959)

Below liq. H_2 temperature down to liq. He temperature, it seems that the protons of NH_3 ligand are rotating or tunneling about three-fold axis in the complex ions of $M(NH_3)_6$ type. Above liq. H_2 temperature, there occurs the molecular reorientation in addition to the rotation or the tunneling of the protons of NH_3 about three-fold axis.

The difference of the line width between the diamagnetic and the paramagnetic salts at room temperature is explained by taking account of the short T_1 in the paramagnetic salts.

The magnitude of the observed shift at low temperature is proportional to the susceptibility and such a relation is derived theoretically by evaluating for three spin system. Comparing each line width and the shift of Co and Mn salts with those of Ni salt, it is suggested that the distance between hydrogen atom and the metal ion in Co and Mn salts is much larger than that in Ni salt. In the measurements on the salts of $Ni(NH_3)_6Cl_2$ and $Ni(NH_3)_6(ClO_4)_2$ at low temperature, there happened an unexpected phenomenon that the proton line disappears suddenly, though the reason of which is not yet certain.

§ 1. Introduction

In many complex salts, they contain H_2O , NH_3 etc. as the coordinate ligands. It seems of interest to study the behavior of these ligands which are in molecular state in the complex salt.

In the present paper, especially, the behavior of NH_3 in the complex salt and the effect of the electron spin on nuclear magnetic resonance were studied by nuclear resonance absorption method. The complex ions under consideration are of $M(NH_3)_6$ type, which forms an octahedron with d^2sp^3 bond between M and six NH_3 . The metal ion M locates at the center of the octahedron, and NH_3 locates at the corners. It may be supposed that three hydrogen atoms in NH_3 locate symmetrically around three-fold axis which joins the centered metal ion to the nitrogen atom. If these hydrogen atoms undertake such a motion as a hindered rotation about three-fold axis, the line of proton magnetic resonance absorption is changed due to this motional effect¹⁾. Accordingly, by studying the temperature variation of the line width and the second moment the present writer intended to investigate the behavior of NH_3 in the complex ion. In the analysis of the line shape caused

by NH_3 , the theoretical calculation for the three spin system is adopted²⁾, and a comparison between calculated and experimental values of the second moment will provide an information concerning a rotational process³⁾. Recently, Murray and Waugh⁴⁾ investigated the structure and molecular motion of the cobalt complex salts by studying the nuclear resonance above liq. air temperature.

In the paramagnetic salts, owing to the interaction between nuclear and electron spins besides the interaction between nuclear spins, the analysis of the line shape is rather complicated than in the diamagnetic salts. Therefore, it was discussed first the behavior of NH_3 in the diamagnetic salts, and then the interaction between nuclear and electron spins in the paramagnetic salts was studied by nuclear resonance by taking account of the results for the diamagnetic salts. The electron spin fluctuates so rapidly by an effect of the short electron spin relaxation time that we may consider the interaction between nuclear spin moment and the time-averaged electron spin moment which is parallel to the magnetic field⁵⁾. Since the time-averaged electron spin moment parallel to the field is given as $\bar{\mu} = \chi_{at}H_0$, where χ_{at} and H_0 are the atomic susceptibility and the field strength respectively, the shift of the absorption line

* Present address: Rigaku-Denki Co., Ltd., X-ray Research Laboratory.

is expected to be proportional to the field strength, and if the atomic susceptibility obeys the Curie law, the shift is inversely proportional to the absolute temperature T . We may expect that, if the atomic susceptibility is known, the unknown distance between the hydrogen atom and metal ion is estimated by observing the line shift.

It is well known that the spin-lattice relaxation time T_1 decreases by a presence of the paramagnetic impurities⁷⁾, and therefore, a short T_1 value is expected in the paramagnetic salts. The line broadening in the paramagnetic salts seems to be caused by such a effect. In applying B.P.P.⁸⁾ equation in such a case, the electron spin relaxation time ρ should be chosen as the correlation time τ_c .

§ 2. Experimental Procedure

(2.1) Apparatus

The block diagram of the apparatus is shown in Fig. (2.1). The measurements were carried out at 15.5 Mc by using an autodyne detector⁹⁾. The signal picked up from an anode circuit of the oscillator and introduced to a narrow band amplifier, was detected by a phase sensitive detector¹⁰⁾. The derivatives of the absorption signal were obtained on the recording millimeter by sweeping the static magnetic field slowly over a required range. The field was swept automatically or manually by supplying the direct current through the

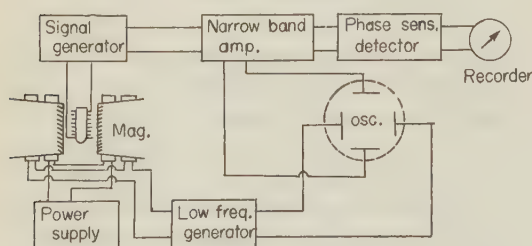


Fig. 2.1. The block diagram of the apparatus.

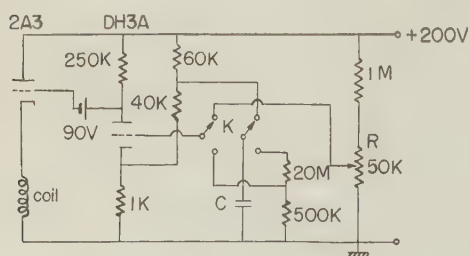


Fig. 2.2. The circuit of the sweeping field.

coil wound separately from the main coil. In the circuit as shown in Fig. (2.2), switching off K , the direct current passing the coil was increased. By replacing the capacitor C for another, the time rate of sweeping field was changed. In manual operation, by sliding the resistor R the strength of the current was changed. The current in the main coil was supplied from the batteries of 120 volts, and the field strength was obtained about 4100 gauss by passing a current of 8 amperes. The pole piece of the electromagnet was 10 cm in diameter with a gap of 4 cm and shimmed to improve the uniformity of the field at the center of the gap¹¹⁾, and the field was modulated by a 30 c.p.s. oscillator⁸⁾. The measurements at low temperature were carried out by using a r.f. spectrometer of Pound-Watkins type¹²⁾.

(2.2) Preparation of the samples

(a) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NH_4Cl was dissolved in water, then we added concentrated aqueous ammonia solution and a small amount of the charcoal to the above solution. After blowing air into the above mixture till the color of the solution changes from red to yellow-brown, it was filtered. The precipitated micro-crystal and charcoal were dissolved in hot concentrated HCl and was filtered. In cooling slowly the solution, the yellow-brown fine micro-crystals of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ were precipitated. The sample was purified by dissolving it in hot concentrated HCl and repeating the above procedure.

(b) $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$

The powdered sample of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ was prepared after reference 13. For the preparation of the single crystal, the powders of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ was dissolved in aqueous ammonia solution to get a saturated solution of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$. A single crystal was recrystallized from the above solution, but the recrystallization was difficult because the solubility of the samples varied with the concentration of ammonia in the solution; the more the concentration of ammonia was decreased, the more the solubility increased. The (111) surface grew comparatively rapid and the single crystal of 10 mm in diameter and of 5 mm thick was obtained.

(c) $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in the aqueous

ammonia solution, and was added the ammonia solution of 2% NH_4ClO_4 . Then, the light blue fine micro-crystals of $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ were precipitated.

(d) $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$, $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$

Each hydrated salt was dehydrated by keeping the temperature above 200°C . The dehydrated salt was kept off from air and let flow the ammonia gas slowly, then we got the powder of pink $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, white $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ and milk-yellow $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$ respectively. These salts were kept in ammonia gas.

$\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$ and $\text{trans-Co}(\text{NH}_3)_4(\text{NO}_2)_2(\text{NO}_3)$ were also used under test.

§ 3. Measurements on Diamagnetic Complex Salts

(3.1) Experimental results

In the measurements at a temperature ranging from liq. He temperature to room temperature, it is found that the line shape is a single peak without any fine structure over the whole temperature range. The observed values of δH and ΔH_2^2 in micro-crystals of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ are given in Table (3.1) and the temperature dependence of δH is shown in Fig. (3.1), where δH and ΔH_2^2 are the line width measured between maximum and minimum slopes and the second moment of the absorption line respectively.

Table III-1.

temp.	$\Delta H_2^2(\text{gauss}^2)$	$\delta H(\text{gauss})$	$T_1(\text{sec.})$
room		3.0	
200°K		3.6	
90°K	17.0	7.5	
60°K	17.5	8.7	
20.4°K	20.1	10	~ 0.03
10°K	20.6	10	~ 0.1
4.2°K	22.0	10	~ 0.5

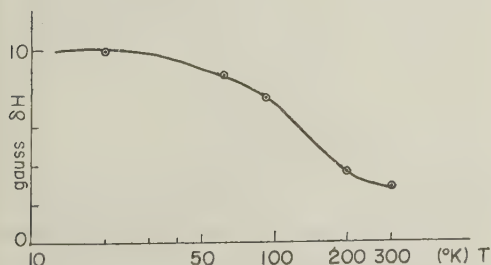


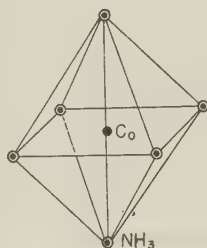
Fig. 3.1. The line width versus temperature in $\text{Co}(\text{NH}_3)_6\text{Cl}_3$.

The relaxation time T_1 values is also shown in Table (3.1). As it seems that T_1 values depend on the purity of the sample, it may be fairly doubtful to consider that T_1 values thus obtained give the definite character of the sample.

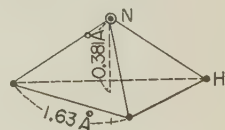
All results for $\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$ are as same as for $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ within the experimental error, and also a same situation holds for $\text{trans-Co}(\text{NH}_3)_4(\text{NO}_2)_2(\text{NO}_3)$, as to the line shape and the line width.

(3.2) Discussion of the results

The structure of $\text{Co}(\text{NH}_3)_6^{3+}$ is as shown in Fig. (3.2) and Co atoms in the unit cell are in the face center cubic symmetry¹⁴⁾. Co-N distance is 1.9 Å and the structure of NH_3 is assumed to be just the same as gaseous NH_3 molecule as shown in Fig. (3.3)¹⁵⁾.



(3.2)



(3.3)

Fig. 3.2. The structure of $\text{Co}(\text{NH}_3)_6^{3+}$.

Fig. 3.3. The structure of NH_3 .

In treating the resonance absorption of protons in NH_3 , the calculation for three spin-system is available. In the absorption line, there are two side peaks on both side of a center peak in rigid lattice, and these side peaks disappear when a motion or tunneling of a triangular configuration of equidistant proton about three-fold axis occurs. In case of triangular rotor, δH can be estimated as follows:

$$\delta H \approx 2 \left(\frac{3}{2} \right) \mu r^{-3} = 9.8 \text{ (gauss)}$$

where μ is the proton magnetic moment and r is the distance between protons. This value is comparable to that observed below liq. H_2 temperature.

We find in Fig. (3.1) that the line width changes over a wide temperature range as like as Murray et al⁴⁾. have pointed out. However, the line width increases as yet below liq. air temperature. Such fact is

contrary to their assumption that the line width at liq. air temperature corresponds to that of protons which are rotating about three-fold Co-N axis. Murray et al. have tried to interpretate the reason of the slow change of the line width above liq. air temperature by assuming the reorientation of two types of the cation, the transition point of which is different. However, the residual motion of NH_3 seems to occur easier rather than the reorientation of the cation.

The second moment in rigid lattice for powdered sample is calculated by using Van Vleck's second-moment formula. For a system rotating about a certain axis, the second moment becomes,

$$(\Delta H_z^2)_{\text{rot}} = 1/4(3 \cos^2 \gamma_{jk} - 1)^2 (\Delta H_z^2)_{\text{rigid}}$$

where γ_{jk} is the angle between r_{jk} and the axis of rotation of r_{jk} , which is the inter-nuclear distance between nuclei j and k . For the system under consideration, since inter-nuclear distance, nuclear spins and g -values are already known, we can compute the second moment in both cases. The calculated value of the second moment due to the dipolar broadening of the protons in a given NH_3 is 38.6 gauss² for rigid and 9.7 gauss² for triangular rotor, and, taking account of the dipolar broadening caused by the protons of another NH_3 and by another nuclei, the total values are ~ 46 gauss² and ~ 14 gauss² for each case respectively. In comparing the second moment in rigid and triangular rotor with the observed values and taking account of the discussion of the line width, we may reasonably conclude that there occurs the hindered rotation or the tunneling of protons in each NH_3 about its three-fold axis below liq. H_2 temperature, and occurs the reorientation of NH_3 as a whole or the cation in addition to the above mentioned motion above liq. H_2 temperature.

§ 4. Measurements on Paramagnetic Complex Salts

In this section we will concern the effect of the electron spin on nuclear resonance absorption in the paramagnetic salts, making use of the knowledge of the behavior, the line width and the line shape of protons in the diamagnetic complex ion which has been discussed in the previous section.

It is of interest to know how the line width and the line shift change with spin number,

and the measurements were carried out on various metal ions of the complex salts of $\text{M}(\text{NH}_3)_6\text{Cl}_2$ type. The Ni^{2+} ion has two unpaired electrons, Co^{3+} and Fe^{2+} , Mn^{2+} ions have three, four and five unpaired electrons respectively.

(4.1) Line width at room temperature

The observed line width at room temperature of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$, $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ are shown in Table (4.1). The values in Table (4.1) are those obtained at a field strength $H_0 = 3700$ gauss, and did not change at $H_0 = 2000$ gauss within experimental error. As seen in the table, these values show nearly the same value with each other. In the above table, the line width of the diamagnetic salt of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ are also included as a reference. Each line shape of these paramagnetic salts is a single peak and the line width shows a quite large value as compared with that of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$.

Table IV-1.

	Samples	δH	$\delta H_{\text{para}} (= \delta H - \delta H_{\text{dia}})$
para	$\text{Ni}(\text{NH}_3)_6\text{Cl}_2$	7.1 gauss	4.1 gauss
	$\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$	7.0	4.0
	$\text{Co}(\text{NH}_3)_6\text{Cl}_2$	6.5	3.5
	$\text{Fe}(\text{NH}_3)_6\text{Cl}_2$	6.9	3.9
	$\text{Mn}(\text{NH}_3)_6\text{Cl}_2$	7.0	4.0
dia	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	3.0	

The difference of the line width between diamagnetic and paramagnetic salts may arise from the unpaired electron in the paramagnetic salts. As we found no large difference in the magnitude of the line width of the paramagnetic salts, it seems that the magnitude of the line width is not much affected by the number of the unpaired electron, or the electron spin number. Such a result may be explained by the following discussion.

In the paramagnetic salts, the proton in NH_3 may be in rotation about three-fold axis as in the diamagnetic salts. It may be considered that the line width consists of two terms, one is due to the mutual interaction among the protons in NH_3 , and the other is due to the unpaired electrons. The former seems to be the same as the line width in the diamagnetic salt and is denoted by δH_{dia} , and

the latter due to the unpaired electrons is denoted by δH_{para} . Then, the line width in the paramagnetic salts may be expressed as,

$$\delta H \approx \delta H_{\text{dia}} + \delta H_{\text{para}}. \quad (4.1)$$

By use of the observed values, $\delta H_{\text{para}} = \delta H - \delta H_{\text{dia}}$ is obtained as about 4 gauss. Of course, in order to express relation (4.1) by the characteristic temperature T_1 and T_2 , it must be considered the line shape. However, we may study the origin of δH_{para} by the order estimation without regard for the line shape.

As the origin of δH_{para} , the contribution due to the distribution of the shift, if exist, to the absorption line may firstly be considered. We may consider such an effect by the following way; the line shift, due to the interaction between electron and nuclear spins, may be expected. However, if the magnitude of the time-averaged magnetic moment is slightly different in each ion, the line will not be equally shifted, and the distribution of the shift contributes to the line width. Next, the contribution of the short T_1 caused by the electron spin to the absorption line, is also regarded as the origin of δH_{para} . The second contribution is to be connected with the second moment due to the electron spin, and will depend on a square of the effective spin moment $\gamma_e^2 \hbar^2 S(S+1)$. By the aid of the calculation in Appendix, as the contribution of the electron spin to the line shift, at room temperature and $H_0 = 3500$, gauss shows the value less than 2 gauss, even in Mn^{2+} in which the magnitude of the electron spin moment is the largest of all the concerned samples, the width due to the distribution of the shift will become too small. Therefore, the first contribution mentioned above is faint, and only the second contribution of the short T_1 on δH_{para} will dominate.

The line width due to the relaxation time T_1 is expressed as,

$$\delta \omega_{\text{para}} \approx 1/T_1$$

where

$$\delta \omega_{\text{para}} = \gamma_p \delta H_{\text{para}}. \quad (4.2)$$

By substituting the observed value of δH_{para} in above expression, we can estimate the T_1 value as $T_1 \sim 10^{-6}$ second.

As the orientation of the nuclear spin in the paramagnetic salt fluctuates by the pre-

sence of the interaction between electron and nuclear spins, B.P.P. equation can also be adopted replacing the electron spin relaxation time ρ for the correlation time τ_c .

$$1/T_1 = 0.9 \hbar^2 \gamma_p^2 \gamma_e^2 S(S+1) \rho \frac{1}{r_{p-e}^6}, \quad (4.3)$$

where γ_p and γ_e are the gyromagnetic ratio of the proton and the electron respectively, and S is the electron spin number, r_{p-e} is the distance between the hydrogen atom and the metal ion. For Ni^{2+} ion, assuming that $\text{Ni}^{2+}-\text{N}$ distance is 1.9 Å, r_{p-e} is estimated as 2.5 Å by use of the data of the crystal structure.

As the origin of the electron spin relaxation time ρ , besides the spin-lattice interaction, the spin-spin and the exchange interaction is also to be taken into account. In order to obtain the T_1 value estimated by using the observed value of δH_{para} , the electron spin relaxation time is to be chosen as $\rho \sim 10^{-10}$ sec. in (4.3). Since the relaxation time due to the spin-lattice interaction is longer than the other two, it is left out of the present discussion. Firstly, the electron relaxation time due to the spin-spin interaction, for which the estimation in order is possible, be considered, and that due to the exchange interaction will be considered later. The frequency deviation due to the electron spin-spin interaction is

$$[\langle \Delta \omega^2 \rangle_{av}]^{1/2} \approx \frac{\gamma_e^2 \hbar \sqrt{S(S+1)}}{\langle r_{e-e}^6 \rangle^{1/2}}. \quad (4.4)$$

Hence, the electron spin-spin relaxation time ρ_s is represented as,

$$\rho_s = \frac{1}{[\langle \Delta \omega^2 \rangle_{av}]^{1/2}} \approx \frac{r_{e-e}^3}{\gamma_e^2 \hbar \sqrt{S(S+1)}}, \quad (4.5)$$

where r_{e-e} is the distance between two metal ions. In Ni^{2+} ion, the distance of the nearest neighbor ion is 7.1 Å and $\rho_s \sim 10^{-10}$ sec. are given by relation (4.5). Over all the samples of Ni, Co, Fe, and Mn salts, if the line shape is of similar type and r_{e-e} is nearly the same, ρ_s is inversely proportional to $\gamma_e^2 \sqrt{S(S+1)}$, and we get from (4.2)

$$\delta H_{\text{para}} \propto \sqrt{S(S+1)} \frac{1}{r_{p-e}^6}. \quad (4.6)$$

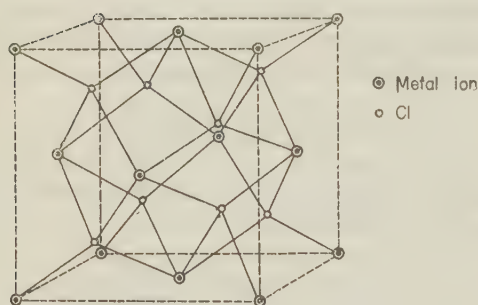
The above result will be easily derived after Anderson's expression for the narrowing of the line width¹⁶⁾

$$\delta\omega \sim \frac{\omega^2}{\omega_p} \approx \frac{r_p^2 r_e^2 \hbar^2 S(S+1)}{r_e^2 \hbar \nu S(S+1)} \frac{r_{e-e}^3}{r_{p-e}^6} \propto \sqrt{S(S+1)} \frac{1}{r_{p-e}^6}, \quad (4.7)$$

where ω^2 is the value of the second moment due to the interaction between nuclear and electron spins on angular frequency scale, and ω_p is the reorientation angular frequency of the electron spin. In above case, the distance between proton and electron spins is assumed to be the same. Such an assumption may be plausible by considering the fact that each of the salt has a similar crystal structure, and the length of the unit cell a_0 is almost the same as seen in Table (4.2)¹⁴. The crystal structure of these salts is the face centered cubic as shown in Fig. (4.1) and the distance of the nearest neighbor ion is that between the corner and the face centered ions.

Table IV-2.

samples	a_0
$\text{NiCl}_2 \cdot 6\text{NH}_3$	10.064 Å
$\text{CoCl}_2 \cdot 6\text{NH}_3$	10.10
$\text{FeCl}_2 \cdot 6\text{NH}_3$	10.14
$\text{MnCl}_2 \cdot 6\text{NH}_3$	10.198

Fig. 4.1. The crystal structure of $\text{M}(\text{NH}_3)_6\text{Cl}_2$.

As we see in Table (4.1), the values of δH_{para} are nearly the same in all samples and do not depend on $\sqrt{S(S+1)}$ as if it seems to contradict to relation (4.6). Such a fact can be reasonably explained by taking the presence of r_{p-e} into account. In comparison of the values of δH_{para} in Co and Ni salts, the former must be 1.4 times as large as that of the latter because of $(\sqrt{S(S+1)})_{\text{Ni}} : (\sqrt{S(S+1)})_{\text{Co}} = 1:1.4$. On the other hand, the ratio of the experimental values of δH_{para} in Co and Ni salts is about 0.85, which fact will

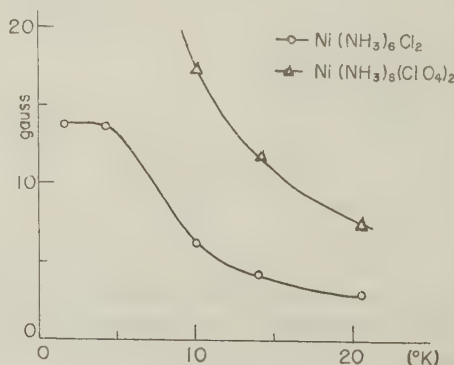
lead us to take in relation (4.6) as $(r_{p-e})_{\text{Ni}} : (r_{p-e})_{\text{Co}} = 0.6:1$. Hence, r_{p-e} in Co salt would be larger than that in Ni salt by an amount of 0.2 Å. Such a fact agrees with the result of the analysis of the crystal structure and it is also considered by comparing relatively the magnitude of the shift of these salts at low temperature. Likewise, in comparison of the values of δH_{para} in Mn and Ni salts, r_{p-e} in Mn salt must be taken about 2.8 Å which is larger than that in Ni salt by an amount of 0.3 Å.

Inspecting the susceptibility data¹⁷), we can find that the exchange interaction exists in these salts except for Mn salt. If the exchange interaction takes an important role in narrowing the line width, the values of δH_{para} in another salts than Mn will become so small comparing with δH_{para} of Mn salt that the effect of the exchange interaction, if exist, is not prominent as compare with that of the spin-spin interaction.

(4.2) Line shift at low temperature

Since the time-averaged electron magnetic moment $\bar{\mu}$ is not large in the field strength of 2000~3000 gauss at room temperature, the contribution due to the interaction between electron and nuclear spins to the first moment of the absorption line has not been taken into account in the previous discussion. At low temperature, however, the magnitude of $\bar{\mu}$ increases as temperature falls and is inversely proportional to the absolute temperature T . Thus, the contribution to the first moment becomes important.

In the field strength of $H_0 = 2000$ gauss, the distinct shift is not observed above liq. air temperature in all salts. In the present ex-

Fig. 4.2. The shifts versus temperature at $H_0 = 2000$ Oe..

periments, the shift of the absorption line was measured comparing with the signal of the proton in water sample which set on near the sample separately.

(4.2 a) $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$

In Fig. (4.2) and (4.3), the temperature and the field dependence of the shift are shown respectively for powdered samples. As seen in Table (4.3), we have found an anomalous phenomenon such that the proton line disappears suddenly at a definite temperature, below which the proton line has not been

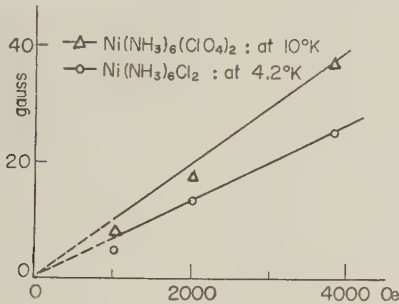


Fig. 4.3. The field dependence of the shift at the constant temperature.

Table IV-3.

Samples	$\text{Ni}(\text{NH}_3)_6\text{Cl}_2$	$\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$
disappear tem. ($^{\circ}\text{K}$)	1.6	~ 7

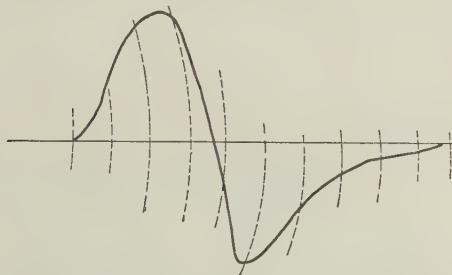


Fig. 4.4a. The derivative curve of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ at 4.2°K .

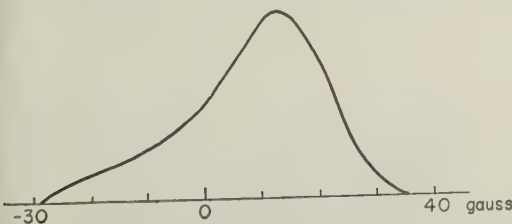


Fig. 4.4b. The line shape of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ obtained from Fig. 4.4a.

observed⁶⁾. Such an anomalous phenomenon above mentioned has occurred in irrespective of the field strength and reversibly in changing the temperature. According to Moriya¹⁸⁾, the spin-lattice relaxation time of proton in a salt in which the spin degeneracy is completely lifted by the crystalline electric field, is expected to increase exponentially below the temperature that is comparable to an interval of the splitting of lowest spin levels. In contrast, the T_1 values of these salts were shorter than 10^{-3} sec. above the temperature below which the proton line was not observed.

As an example, the proton line of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ at 4.2°K is shown in Fig. (4.4). The line draws a long tail on the side of the low field and is cut on the other side. For a powdered sample of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, the color of the sample was also examined by using the glass cryostat near the temperature at which the proton line disappears, but the change in the color of the sample was not observed in a temperature range from 1.5°K to liq. H_2 temperature.

For the single crystal of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, the proton line disappeared also at 1.6°K just the same as for powder. Applying the field in [111] direction the single peak without shift was observed and when the field was applied in [100] direction the line separated in two peaks at 4.2°K . The width between these two peaks was about 15 gauss at $H_0=2000$ gauss and it decreases in nearly a half at $H_0=1000$ gauss.

(4.2 b) $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$

As in Ni salts, the shift of the absorption line was observed at low temperature as shown in Fig. (4.5). The line was broadened with increase of the shift, and it is hard to catch exactly the center of the shifted line. In Mn salt, it showed the larger shift and the

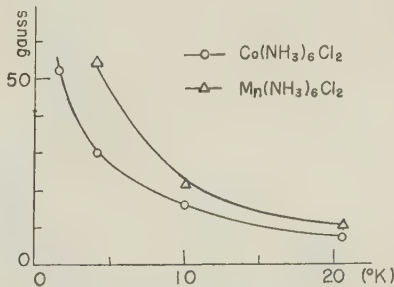


Fig. 4.5. The shifts versus temperature at $H_0=2000 \text{ Oe.}$

line was more broadened, hence, the shift was not measured below liq. He temperature. In these salts, such an anomalous phenomenon occurred in Ni salts was not observed over the whole temperature range.

(4.3) Calculation of the line shape and the shift

For a system concerned with, the elements of a secular determinant is calculated by using the wave function of three spin system as seen in Appendix, when three spins couple with each other. The secular determinant is consisted of two parts and each of them is four column determinant. In a rotating system, non-diagonal elements vanish and the energy term is easily calculated. The component line of the powdered sample of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ at $H_0=2000$ gauss is derived from the calculated energy diagram and is shown in Fig. (4.6). It seems that the maximum region of the component line corresponds to the center of the observed shift.

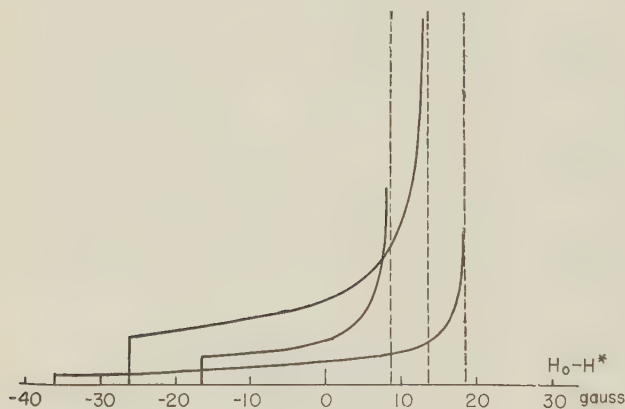


Fig. 4.6a. Each component line.

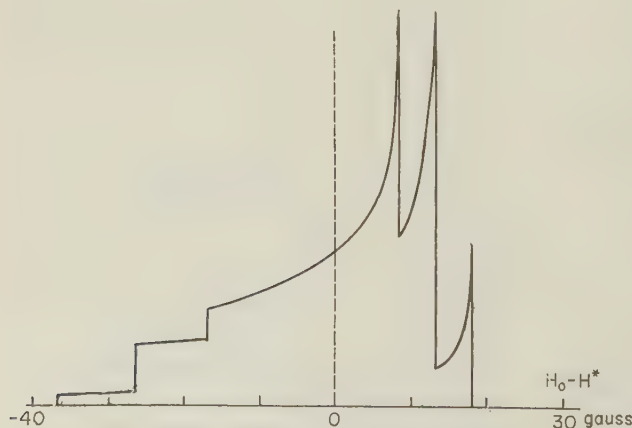


Fig. 4.6b. The composed component line.

When the interaction between nuclear and electron spins becomes larger than that between nuclear spins, the nuclear spin will couple with the electron spin directly. For the decoupled system mentioned, the energy diagram is also calculated and shows the centered component line shifted by same quantity as for the coupled three spin system. However, as the mode of the dipolar interaction of nuclear spins and the transition probability between the energy levels differ from that in the coupled system, the line shape is slightly different.

For a single crystal, applying the field in [111] direction, the angular factor $(3 \cos^2 \theta - 1)$ of the perturbing energy reduces to zero and the line without shift is to be observed. When the field is applied in [100] direction, NH_3 in a complex ion may be classified into two groups. In Fig. (4.7), a and b form a group of which line shifts to the high field and c, d, e and f form another group of which line shifts to the low field. The observed line in the single crystal of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ seems to be composed of these two parts.

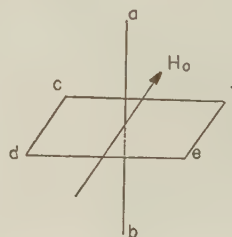


Fig. 4.7. The groups of NH_3 in $\text{Ni}(\text{NH}_3)_6^{2+}$.

(4.4) Comparison of the line shift and the magnetic susceptibility

As the shift is proportional to the time averaged moment, namely proportional to the magnetic susceptibility at $H_0=\text{const.}$, in both coupled and decoupled system (see Appendix), the comparison of the shift with the susceptibility may be undertaken. In order to compare the shift with the susceptibility data, the curve of the molar susceptibility versus temperature obtained by Kido and Watanabe¹⁷⁾ is quoted in Fig. (4.8).

For each salt, the temperature dependence of the shift shows the similar behavior as that of the molar suscep

tibility as seen in Fig. (4.2), (4.5) and (4.8). Comparing the shift of $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ and $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, at 10°K , it turns out the shift of $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ is larger than that of $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ in a ratio of 1.1:1 on the contrary to the fact that the molar susceptibility of the latter is larger than that of the former. But, assuming r_{p-e} in $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ is larger than that in $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ by an amount of $0.2 \text{ \AA}$ as was given in previous section, the difference of the observed shift can be well explained. However, the ratio of the shift in $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ is smaller than that of the expected shift from the susceptibility data even though r_{p-e} in Mn salt is larger than that in Ni salt by an amount of $0.3 \text{ \AA}$ as was given in previous section (compare Fig. (4.5) and Fig. (4.8)).

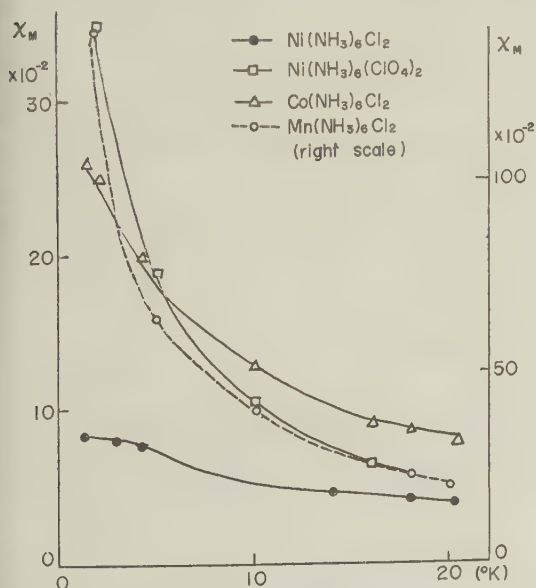


Fig. 4.8. The molar susceptibility versus temperature.

In this case, since it is hard to assume that r_{p-e} in $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ would be still larger by an amount to account for the difference of the shift, the discrepancy may not be simply explained by the difference of r_{p-e} in these salts.

§ 5. Conclusion

The behavior of NH_3 was investigated in the diamagnetic complex salts, and the observed line width and the shift of the absorption line in the paramagnetic salts were explained by the interaction between nuclear

and electron spins based on the observed results in the diamagnetic salts. In comparison of the line width in each salt at room temperature and that of the shift and the susceptibility at low temperature, the difference in the distance between hydrogen atom and metal ion was estimated.

The mode of the temperature dependence of the shift is similar to that of the susceptibility. However, in Ni salts at low temperature, the absorption line disappeared and the shift could not be observed in spite of the fact that the susceptibility could be measured continuously. The paramagnetic resonance could not be observed in these Ni salts. Recently, for $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, Date¹⁹⁾ observed the paramagnetic resonance above 74°K , and below which he could not observe the resonance line because of the disappearance of the resonance line. It may be concluded that the proton line can not be observed because of either a sudden increase of T_1 or a sudden broadening of the line.

Acknowledgement

The author wishes to express his hearty gratitude to Professor K. Kido and Assistant Professor I. Kanomata for their kind guidance and encouragement throughout the present work. The author is also grateful to Mr. T. Watanabe, who supplied to him the susceptibility data before publication and gave him kind advice for preparation of the sample, and to Dr. T. Sugawara of the Research Institute for Iron, Steel and Other Metals of Tohoku University who afforded him facilities to do the experiment at low temperature in using his apparatus and give him many valuable suggestions for present work.

Appendix

Taking into account of the interaction between nuclear and electron spin, a calculation of the energy term of three spin system is carried out and the magnitude of the shift in the paramagnetic salt is derived. Firstly, the coupled three spin system is taken under consideration.

The effective Hamiltonian for this system is

$$H_{\text{eff}} = g\beta H_0 \sum_{j=1}^3 I_{zj} + \sum_{j>j'} (I_j I_{k'} - 3I_{zj} I_{zj'}) A_{jk} - \sum_j I_{zj} B_j = H^0 + H^1, \quad (1)$$

where

$$\left. \begin{aligned} A_{jk} &= \frac{1}{2} g^2 \beta^2 r_{jk}^{-3} (3 \cos^2 \theta_{jk} - 1), \\ B_j &= g \beta (g_e \beta_e S_z) r_j^{-3} (3 \cos^2 \theta_j - 1) \\ &= g \beta \bar{\mu} (3 \cos^2 \theta_j - 1) r_j^{-3}. \end{aligned} \right\} \quad (2)$$

and

$$H^{(1)} = \sum_{j>j'} (I_j I_k - 3 I_{zj} I_{zk}) A_{jk} - \sum_j I_{zj} B_j$$

r_{jk} and r_j are the distance between nuclei j and k , and that between nuclei j and the

metal ion respectively. θ_{jk} and θ_j are the angle between r_{jk} and the field strength H_0 , and that between r_j and H_0 . $I_{zj} B_j$ is the interaction between nuclear and electron spin. According to Bersohn²⁾, the states of such three spin system labelled by the eigenvalue of J^2 , I^2 and I_z where $J = I_1 + I_2$, $I = J + I_3$ and $I_z = I_{1z} + I_{2z} + I_{3z}$. Then, the secular determinant is

$$\begin{vmatrix} M_I = \frac{3}{2} & I = \frac{3}{2} & -2x - \frac{1}{2}(B_1 + B_2 + B_3) \\ M_I = \frac{1}{2} & I = \frac{3}{2} & 2x - \frac{1}{6}(B_1 + B_2 + B_3) & a - \frac{1}{\sqrt{6}}(B_1 - B_2) & b - \frac{1}{3\sqrt{2}}(2B_3 - B_1 - B_2) \\ I = \frac{1}{2} & J = 0 & a - \frac{1}{\sqrt{6}}(B_1 - B_2) & -\frac{1}{2} B_3 & -\frac{1}{\sqrt{12}}(B_1 - B_2) \\ I = \frac{1}{2} & J = 1 & b - \frac{1}{3\sqrt{2}}(2B_3 - B_1 - B_2) & -\frac{1}{\sqrt{12}} & -\frac{1}{6}(2B_1 + 2B_2 - B_3) \end{vmatrix}$$

where

$$x = \frac{1}{4} (A_{12} + A_{23} + A_{13}), \quad b = \frac{\sqrt{2}}{4} (2A_{12} - A_{13} - A_{23}), \quad a = \frac{\sqrt{6}}{4} (A_{13} - A_{23}). \quad (3)$$

For $M_L < 0$, the elements of matrix is calculated by a same procedure as for $M_I > 0$. The diagonal elements of matrix for $M_I < 0$ is

$$-2x + 1/2(B_1 + B_2 + B_3), \quad 2x + 1/6(B_1 + B_2 + B_3), \quad 1/2 B_3, \quad 1/6(2B_1 + 2B_2 - B_3), \quad (4)$$

For the rotational system, using the addition theorem of spherical harmonics

$$\langle 3 \cos^2 \theta_{jk} - 1 \rangle_\phi = 1/2 (3 \cos^2 \theta - 1) \cdot (3 \cos^2 \gamma_{jk} - 1),$$

The subscript ϕ denotes an average over the azimuthal angle, and γ_{jk} is the angle between r_{jk} and the axis of rotation of r_{jk} . In the present case under consideration,

$$\cos \gamma_{jk} = 0,$$

$$\langle 3 \cos^2 \theta_{jk} - 1 \rangle_\phi = \frac{1}{2} (1 - 3 \cos^2 \theta),$$

and

$$x = 1/4 (A_{12} + A_{23} + A_{13}) = 3/16 g^2 \beta^2 (1 - 3 \cos^2 \theta) r^{-3}, \quad (5)$$

where θ is the angle between the external magnetic field and the normal to the plane of

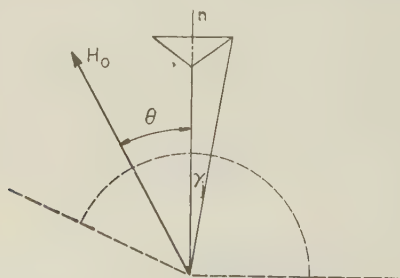


Fig. 1. Diagram defining θ and γ_j .

the triangle,

Likewise

$$\langle 3 \cos^2 \theta_j - 1 \rangle_\phi = \frac{1}{2} (3 \cos^2 \theta - 1) \cdot (3 \cos^2 \gamma_j - 1), \quad (6)$$

where γ_j is the angle between r_j and the axis of rotation of r_j . Accordingly, by putting the following relation, B is expressed as follows,

$$B_1 = B_2 = B_3 = -B,$$

$$B = \frac{1}{2} g \beta \bar{\mu} (3 \cos^2 \gamma_j - 1) \cdot (1 - 3 \cos^2 \theta) r_{j-e}^{-3}.$$

In case of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, $\cos \gamma_j = 2.3/2.5$ from the crystal structure, and $\bar{\mu} = 53 \beta_{\text{nuc}}$ at 4.2°K and $H_0 = 2000$ gauss by using the susceptibility data, where β_{nuc} is the nuclear magneton. For the rotational system, non-diagonal terms vanish and the secular determinant becomes

$$\begin{vmatrix} -2x + \frac{3}{2} B & 0 & 0 \\ 0 & 2x + \frac{1}{2} B & 0 \\ 0 & 0 & \frac{1}{2} B \\ 0 & 0 & 0 & \frac{1}{2} B \end{vmatrix}. \quad (7)$$

In Fig. (2), the energy diagram and the al-

lowed transition were shown taking account of the selection rule $\Delta J=0$, $\Delta I=0$ and $\Delta M_I=\pm 1$.

For the transition $-1/2 \rightarrow -3/2$

$$h\nu = g\beta H_0 - (B + 4x).$$

Substituting $h = g\beta H^*$, the resonance value for the external field is obtained as,

$$-1/2 \rightarrow -3/2, \quad H_0 = H^* + \frac{1}{g\beta} (B + 4x).$$

In the same way

$$\left. \begin{aligned} 1/2 \rightarrow -1/2 \quad H_0 &= H^* + \frac{1}{g\beta} B, \\ 3/2 \rightarrow 1/2 \quad H_0 &= H^* + \frac{1}{g\beta} (B - 4x). \end{aligned} \right\} \quad (8)$$

When the interaction between nuclear and electron spin becomes larger than that of nuclear spins, the nuclear spin couples with the electron spin directly. For this decoupled system, when the protons in NH_3 rotate about three-fold axis, each proton shows the same diagram as shown in Fig. (3), where the same abbreviation used in the coupled system is adopted. The resonance value for the external field is obtained as,

$$\left. \begin{aligned} H_0 &= H^* + \frac{1}{g\beta} (B + \frac{2}{3} \cdot 4x), \\ H_0 &= H^* + \frac{1}{g\beta} B, \\ H_0 &= H^* + \frac{1}{g\beta} (B - \frac{2}{3} \cdot 4x). \end{aligned} \right\} \quad (9)$$

In both cases, the line shift is proportional to

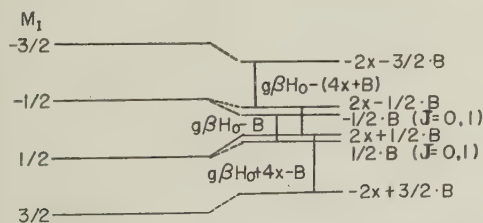


Fig. 2. Energy diagram for the coupled three spin system.

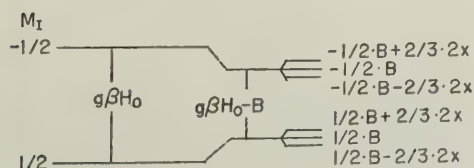


Fig. 3. Energy diagram for the decoupled system.

B term. In each case, taking into account of each transition probability, we can obtain the composed component line.

For the single crystal of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, applying the field in $[111]$ direction, the angular factor $(1 - 3\cos^2\theta)$ reduces to zero because of $\cos\theta = 1/\sqrt{3}$, and applying the field in $[100]$ direction, the angular factor becomes as follows,

for c, d, e and f in Fig. (4.7)

$$1 - 3\cos^2\theta = -1/2.$$

for a and b in Fig. (4.7)

$$1 - 3\cos^2\theta = 1.$$

Hence, the line of a and b shifts to the high field and that of c, d, e and f shifts to the low field. Thus, the total component line has two side peaks.

References

- 1) R. Kubo and K. Tomita: J. Phys. Soc. Japan **9** (1954) 888. N. Bloembergen, E. M. Purcell and R. V. Pound: Phys. Rev. **73** (1948) 679.
- 2) E. R. Andrew and R. Bersohn: J. Chem. Phys. **18** (1950) 159.
- 3) H. S. Gutowsky and G. E. Pake: J. Chem. Phys. **18** (1950) 162.
- 4) G. R. Murray and J. S. Waugh: J. Chem. Phys. **29** (1958) 207.
- 5) K. Kambe and T. Usui: Progr. Theor. Phys. **8** (1952) 302.
- 6) P. H. Kim and T. Sugawara: J. Phys. Soc. Japan **13** (1958) 968.
- 7) J. H. Van Vleck: Phys. Rev. **74** (1948) 61. N. Bloembergen, E. M. Purcell and R. V. Pound: op. cit.
- 8) N. Bloembergen: *Nuclear Magnetic Relaxation* (The Hague: Nijhoff, 1948).
- 9) H. Shono: R. I. Sci. and Tech. University of Tokyo **6** (1952) 201 (In Japanese).
- 10) N. A. Schuster: Rev. Sci. Inst. **22** (1951) 254.
- 11) M. E. Rose: Phys. Rev. **53** (1938) 715.
- 12) G. Watkins: Thesis, Harvard University (1953). T. Sugawara: Sci. Rep. RITU **A-8** (1956) 95.
- 13) K. Kido and T. Watanabe: to be published in J. Phys. Soc. Japan.
- 14) R. W. G. Wyckoff: *Crystal Structures II*, (Intersci. Publ., 1951).
- 15) G. Herzberg: *Molecular Spectra and Molecular Structure II*, (D. Van Nostrand Company, 1945).
- 16) P. W. Anderson and P. R. Weiss: Rev. Mod. Phys. **25** (1953) 269.
- 17) K. Kido and T. Watanabe: to be published.
- 18) T. Moriya: J. Phys. Soc. Japan **13** (1958) 1344.
- 19) M. Date: private Communication.

On the Magnetic Susceptibility of FeF_2^* .

By Akio HONMA

*Department of Physics,
Tokyo University of Education, Tokyo, Japan*

(Received October 3, 1959)

Adopting the effective Hamiltonian by Pryce and the molecular field approximation, the parallel and perpendicular susceptibilities of FeF_2 are calculated. According to the experiments by Stout and Matarrese, the perpendicular susceptibility below the Néel point decreases with decreasing temperature. Denoting the components of the D -tensor in Pryce's effective Hamiltonian by D_i ($i=x, y, z$) where the z -axis is taken as the c -axis and the x -axis as the direction of the line connecting two nearest neighbouring F ions, this behaviour of the perpendicular susceptibility can be explained if $Dx, Dy > Dz$. The parallel susceptibility at absolute zero has a non-zero value proportional to $(Dx - Dy)^2$. However this term is of the same or small order compared with the temperature-independent part of the magnetic susceptibility. Comparisons with experiments are made by using the values of the D -tensor and the g -factor obtained by Tinkham. If the reasonable values of exchange integrals are adopted, the calculated susceptibilities are in good agreement with the experimental results by Stout and Matarrese.

§ 1. Introduction

The crystal of FeF_2 has the rutile structure and is antiferromagnetic. Its Néel point is 78.3°K from the specific heat measurements.¹⁾ The magnetic anisotropy was studied experimentally by Stout and Matarrese²⁾ over the temperature range 10°~300°K. Using the data of the powder susceptibility measured by Bizette and Tsai³⁾, they obtained the individual susceptibilities perpendicular and parallel to the c -axis, $\chi_\perp$ and $\chi_\parallel$. Since the powder data do not extend below 63°K, the portions of the curves below this temperature can not be determined. According to them, however, $\chi_\perp$ below the Néel point decreases with decreasing temperature. To obtain the individual curves below 63°K, Stout et al. made extrapolations based upon the assumption that the parallel susceptibility approaches zero at 0°K. The value of $\chi_\perp$ extrapolated to 0°K is about 0.9 times its value at the Néel point. Further they obtained that $\chi_\parallel - \chi_\perp$ at hydrogen temperatures is proportional to the fourth power of temperature.

The theoretical investigations of the magnetic anisotropy were undertaken by Niira and Oguchi⁴⁾ and by Moriya, Motizuki, Kana-

mori and Nagamiya⁵⁾. In particular, Moriya et al. calculated directly the crystalline electric field itself and they obtained the magnetic anisotropy by taking account of the spin-orbit coupling. According to Abragam and Pryce⁶⁾, when the lowest orbital state of a paramagnetic ion is a singlet and the energy separation between the lowest and the first excited levels is much greater than the magnitude of the spin-orbit coupling constant λ , the effective Hamiltonian pertaining to the lowest orbital state of this ion is given by

$$\mathcal{H} = \mathcal{H}_a + \mathcal{H}_f, \quad (1.1)$$

$$\mathcal{H}_a = D_x S_x^2 + D_y S_y^2 + D_z S_z^2, \quad (1.1a)$$

$$\begin{aligned} \mathcal{H}_f = & \mu_0 (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) \\ & - \mu_0^2 (A_x H_x^2 + A_y H_y^2 + A_z H_z^2), \end{aligned} \quad (1.1b)$$

in the presence of an external magnetic field $\mathbf{H}$, where the coordinate system is taken so as to agree with the symmetrical axes of the crystalline electric field and g_i and A_i are given by

$$g_i = 2(1 - \lambda A_i), \quad (1.2)$$

$$A_i = \sum_n \frac{| \langle o | L_i | n \rangle |^2}{E_n - E_o}. \quad (1.3)$$

and S is the usual spin operator, L the orbital angular momentum operator, μ_0 the Bohr magneton and o, n refer to the lowest and excited orbital states. The D -tensor for Fe

* Submitted in partial fulfillment of the requirements for the D.S degree in the Tokyo University of Education.

ion arises from the two main sources: one is the spin-orbit coupling and the other the spin-spin interaction within the ion. If the latter can be neglected, the D -tensor is given by

$$D_i = -\lambda^2 A_i. \quad (1.4)$$

Moriya et al. calculated the A -tensor. Using these results and the molecular field approximation, they showed that the calculated susceptibility in the paramagnetic region is in fairly good agreement with the experimental one.

Tinkham⁷⁾ has performed the measurements of the paramagnetic resonance on the various iron-group elements included in ZnF_2 as impurities and offered the valuable informations about these ions. As to Fe ions, he obtained the energy separation, ΔE , between the lowest and the next levels of (1.1a) and the g -factor with respect to the c -axis. According to these results, ΔE is much smaller than that calculated by Moriya et al., thus the effective Hamiltonian (1.1a) has the nearly tetragonal symmetry. However it should be remarked that the D -tensor obtained by him contains a significant contribution from the spin-spin interaction. Though his data were obtained as to Fe ions included in ZnF_2 as impurities, it may be said that his data give the fairly reliable informations about Fe ions in FeF_2 , because the differences of lattice constants between ZnF_2 and FeF_2 are small.

In this paper we shall calculate the magnetic susceptibility, by using the effective Hamiltonian (1.1) and the molecular field approximation to describe the exchange coupling among spins. In particular we shall study in detail the perpendicular susceptibility below the Néel point and investigate under what condition the experimental behaviour can be explained. Further we shall compare the calculated susceptibility with the experimental one, by adopting the data by Tinkham and reasonable exchange integrals.

§ 2. Eigenvalues of the Effective Hamiltonian

In this crystal the metallic ions constitute a body-centred tetragonal lattice. According to the experiments of neutron diffraction⁸⁾, the spin alignment below the Néel point is along the c -axis. We shall take the c -axis as the z -axis and the direction of the line connecting

two nearest neighbouring F ions as the x -axis, and denote the spins on the body-centre sites by $S^{(1)}$ and those on the corner sites by $S^{(2)}$. Using (1.1) and the molecular field approximation to describe the exchange coupling $2\sum J_{ij} S_i \cdot S_j$, the effective Hamiltonian for the spins on the body-centre sites is then written

$$\mathcal{H}_0^{(1)} = \mathcal{H}_a^{(1)} + \mathcal{H}_{ex}^{(1)}, \quad (2.1)$$

$$\mathcal{H}_a^{(1)} = -D_1 S_z^{(1)2} - D_2 S_x^{(1)2}, \quad (2.1a)$$

$$\mathcal{H}_{ex}^{(1)} = (2z_1 J_1 \langle S_z^{(2)} \rangle + 2z_2 J_2 \langle S_z^{(2)} \rangle S_z^{(1)} - k\alpha \langle S \rangle S_z^{(1)}), \quad (2.1b)$$

in the absence of the external magnetic field, where D_1 and D_2 are $D_y - D_z$ and $D_y - D_x$ respectively, J_1 , J_2 the exchange integrals between nearest neighbours and between second neighbours, $z_1 (=2)$, $z_2 (=8)$ the numbers of the nearest and second neighbours, $\langle S \rangle$ the average of $S_z^{(1)}$ i.e. the spontaneous magnetization and $k\alpha$ is thus written as

$$k\alpha = -2z_1 J_1 + 2z_2 J_2. \quad (2.2)$$

k being the Boltzmann factor. The Hamiltonian for the spins on the corner sites is obtained by interchanging x , y with y , x . Using the spin functions of $S=2$, the Hamiltonian (2.1) is represented by the following form:

$$\mathcal{H}_0 = \begin{vmatrix} A_1 - k\alpha \langle S \rangle & B & & \\ & & O & \\ B & A_1 + k\alpha \langle S \rangle & & \\ & A_2 - 2k\alpha \langle S \rangle & C & O \\ O & C & A_3 & C \\ & O & C & A_2 + 2k\alpha \langle S \rangle \end{vmatrix} \quad (2.3)$$

where

$$\begin{aligned} A_1 &= -D_1 - \frac{5}{2} D_2, & B &= -\frac{3}{2} D_2, \\ A_2 &= -4D_1 - D_2, & C &= -\left(\frac{3}{2}\right)^{1/2} D_2, \\ A_3 &= -3D_2, \end{aligned} \quad (2.3a)$$

The roots of the secular equation of (2.3) are

$$\begin{aligned} E_1 &= A_1 - \{(k\alpha \langle S \rangle)^2 + B^2\}^{1/2}, \\ E_2 &= A_1 + \{(k\alpha \langle S \rangle)^2 + B^2\}^{1/2}, \\ E_3 &= -2r^{1/3} \cos \frac{\varphi - \pi}{3} + \frac{2A_2 + A_3}{3}, \\ E_4 &= 2r^{1/3} \cos \frac{\varphi}{3} + \frac{2A_2 + A_3}{3}, \end{aligned} \quad (2.4)$$

$$E_5 = -2r^{1/3} \cos \frac{\varphi + \pi}{3} + \frac{2A_2 + A_3}{3},$$

where if we define

$$a = \frac{1}{3}(16D_1^2 - 16D_1D_2 + 13D_2^2) + (2k\alpha\langle S \rangle)^2, \quad (2.5)$$

$$b = \frac{2}{3}(2D_1 - D_2)\{2(2k\alpha\langle S \rangle)^2 - \frac{1}{9}(32D_1^2 - 32D_1D_2 + 35D_2^2)\}, \quad (2.6)$$

then

$$r^{1/3} = \left(\frac{a}{3}\right)^{1/2}, \quad \cos \varphi = -\frac{b}{2r}. \quad (2.7)$$

In order to refine the following equation, we introduce the orthogonal transformation matrix $\mathfrak{U}$ which diagonalizes $\mathcal{H}_0$. This matrix is defined by

$$\mathfrak{U} = (a_{ij}), \quad i, j = 1, 2, 3, 4, 5. \quad (2.8)$$

and a_{ij} can be obtained easily from (2.3) and (2.4) as follows:

$$\frac{a_{i2}}{a_{i1}} = \frac{E_i + k\alpha\langle S \rangle - A_1}{B}, \quad a_{i1}^2 + a_{i2}^2 = 1, \quad \text{for } i = 1, 2,$$

$$\frac{a_{j4}}{a_{j3}} = \frac{E_j + 2k\alpha\langle S \rangle - A_2}{C}, \quad \frac{a_{j5}}{a_{j3}} = \frac{E_j + 2k\alpha\langle S \rangle - A_2}{E_j - 2k\alpha\langle S \rangle - A_2}$$

$$a_{j3}^2 + a_{j4}^2 + a_{j5}^2 = 1, \quad \text{for } j = 3, 4, 5. \quad (2.9)$$

$$a_{kl} = a_{lk} = 0, \quad \text{for } k = 1, 2; \quad l = 3, 4, 5.$$

In the temperature range of $T \geq T_N$, $\langle S \rangle$ takes the value of zero. Therefore the matrix $\mathfrak{U}$ is simplified as

$$\mathfrak{U} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1 & -1 & 0 & & \\ 1 & 1 & & & \\ & \cos \theta & -\sqrt{2} \sin \theta & \cos \theta & \\ 0 & \sin \theta & \sqrt{2} \cos \theta & \sin \theta & \\ & -1 & 0 & 1 & \end{vmatrix}, \quad (2.10)$$

with

$$\tan 2\theta = -\sqrt{3} D_2 / (2D_1 - D_2). \quad (2.10a)$$

§ 3. Magnetic Susceptibility

3a) The parallel magnetic susceptibility

We consider the case where the external magnetic field is along the z -axis. Since both the body-centre and the corner sites are equivalent with respect to the z -axis, we do not make the distinction between them. The Hamiltonian is written as

$$\mathcal{H} = \mathcal{H}_0 + \delta_1 S_z - \mu_0^2 A_z H_z^2, \quad (3.1)$$

$$\delta_1 = \mu_0 g_z H_z + k\gamma \langle \delta S_z \rangle, \quad (3.1a)$$

where $\mathcal{H}_0$ is Eq. (2.1), $\langle \delta S_z \rangle$ the average of

the spin component induced by the external magnetic field and $k\gamma$ is defined by

$$k\gamma = 2z_1 J_1 + 2z_2 J_2. \quad (3.2)$$

The last term of the Hamiltonian, which is spin-independent and quadratic in H_z , gives a temperature-independent susceptibility and so may be added after the other terms were calculated. The self-consistent relation is written as

$$\langle S \rangle + \langle \delta S_z \rangle = Tr S_z e^{-\beta \mathcal{H}} / Tr e^{-\beta \mathcal{H}}, \quad (3.3)$$

where β means $1/kT$. Using the relation

$$e^{-\beta(a+b)} = e^{-\beta a} - \int_0^\beta e^{-(\beta-s)a} b e^{-s a} ds + \dots \quad (3.4)$$

the right hand side of (3.3) can be expanded into powers of H_z . Its zeroth order term gives the spontaneous magnetization of sublattices,

$$\langle S \rangle = \left\{ \sum_{i=1,2} (a_{i1}^2 - a_{i2}^2) \exp(-\beta E_i) + 2 \sum_{j=3,4,5} (a_{j3}^2 - a_{j5}^2) \exp(-\beta E_j) \right\} / Z, \quad (3.5)$$

with $Z = Tr \exp(-\beta \mathcal{H}_0)$ and the first order term in (3.3) is the induced spin component:

$$\langle \delta S_z \rangle = -P\delta_1, \quad (3.6)$$

where

$$ZP = 8 \{ a_{11}^2 a_{12}^2 t_{12} + \sum_{\substack{i < j \\ (3,4,5)}} (a_{i3} a_{j3} - a_{i5} a_{j5})^2 t_{ij} \} + \beta \{ \sum_{i=1,2} (a_{i1}^2 - a_{i2}^2)^2 \exp(-\beta E_i) + 4 \sum_{j=3,4,5} (a_{j3}^2 - a_{j5}^2)^2 \exp(-\beta E_j) - Z \langle S \rangle^2 \}. \quad (3.7)$$

Here

$$t_{ij} = \frac{\exp(-\beta E_i) - \exp(-\beta E_j)}{E_j - E_i}. \quad (3.8)$$

$\langle S \rangle = 0$ is always the solution of (3.5), but the non-zero solution of $\langle S \rangle$ is stable in the region below the Néel point. At absolute zero the lowest energy level is E_3 , as one sees from (2.4). Therefore the spontaneous magnetization of sublattices at 0°K is given by

$$\langle S \rangle_0 = 2(a_{33}^2 - a_{35}^2). \quad (3.9)$$

which is obtained by taking the limit of $\beta \rightarrow \infty$ in (3.5). This means that $\langle S \rangle_0$ shrinks from its maximum value 2 by reason of the fact that S_z is not commutable with $\mathcal{H}_0$. Therefore $2 - \langle S \rangle_0$ should be proportional to D_2^2 .

From (3.9) with (3.1a), $\langle \delta S_z \rangle$ can be obtained. As the average magnetic moment induced by the external magnetic field is given by $-\mu_0 g_z \langle \delta S_z \rangle$, we get the expression for $\chi_{\parallel}$ after adding the temperature-independent

susceptibility:

$$\chi_{\parallel} = N\mu_0^2 g_z^2 P / (1 + k\gamma P) + 2N\mu_0^2 A_z. \quad (3.10)$$

At the absolute zero of temperature, P has a non-zero value P_0 which can be obtained from (3.7) by taking the limit of $\beta \rightarrow \infty$:

$$P_0 = 8 \left\{ \frac{(a_{33}a_{43} - a_{35}a_{45})^2}{E_4 - E_3} + \frac{(a_{33}a_{53} - a_{35}a_{55})^2}{E_5 - E_3} \right\}. \quad (3.11)$$

This arises from the fact that the perturbing Hamiltonian is not commutable with the unperturbed one. Therefore P_0 should be proportional to D_z^2 . In the temperature range of $T \geq T_N$, P is written, by using (2.10), as

$$Z'P = 2(t_{12} + 4t_{35} \cos^2 \theta + 4t_{45} \sin^2 \theta). \quad (3.12)$$

with $Z' = \text{Tr} \exp(-\beta \mathcal{H}_a)$. (3.12) corresponds to the formula obtained by Moriya et al.

The exchange parameter $k\alpha$ defined by (2.2) can be determined by P at the Néel point. Expanding the right hand side of (3.5) with respect to $\langle S \rangle$, we get the relation

$$k\alpha = 1/P_N. \quad (3.13)$$

3b) The perpendicular magnetic susceptibility

For the sake of simplicity we consider the case where the external magnetic field is parallel to the x -axis. Since the x - and y -axes differ by 90° rotations from the body-centre to the corner sites, the Hamiltonian for $S^{(1)}$ and $S^{(2)}$, except for the terms which give the temperature-independent susceptibilities, are written as

$$\begin{aligned} \mathcal{H}^{(1)} &= \mathcal{H}_0^{(1)} + \delta_2 S_x^{(1)}, \\ \mathcal{H}^{(2)} &= \mathcal{H}_0^{(2)} + \delta_3 S_x^{(2)}, \end{aligned} \quad (3.14)$$

with

$$\begin{aligned} \delta_2 &= \mu_0 g_x H_x + 2z_1 J_1 \langle \delta S_x^{(1)} \rangle + 2z_2 J_2 \langle \delta S_x^{(2)} \rangle, \\ \delta_3 &= \mu_0 g_y H_x + 2z_1 J_1 \langle \delta S_x^{(2)} \rangle + 2z_2 J_2 \langle \delta S_x^{(1)} \rangle, \end{aligned} \quad (3.14a)$$

where $\langle \delta S^{(1)} \rangle$ and $\langle \delta S_x^{(2)} \rangle$ are the average spin changes induced by the external magnetic field. From the self-consistent relations

$$\begin{aligned} \langle \delta S_x^{(i)} \rangle &= \text{Tr} S_x^{(i)} \exp(-\beta \mathcal{H}^{(i)}) / \\ &\quad \text{Tr} \exp(-\beta \mathcal{H}^{(i)}), \quad i=1, 2. \end{aligned} \quad (3.15)$$

we can obtain $\langle \delta S_x^{(i)} \rangle$. Using the formula (3.4), we have (3.15) as the expanded forms:

$$\begin{aligned} \langle \delta S_x^{(1)} \rangle &= -Q\delta_2, \\ \langle \delta S_x^{(2)} \rangle &= -R\delta_3, \end{aligned} \quad (3.16)$$

where

$$\begin{aligned} ZQ &= 2 \sum_{i=3,4,5} [\{a_{11}(a_{i3} + \sqrt{3/2} a_{i4}) \\ &\quad + a_{12}(a_{i5} + \sqrt{3/2} a_{i4})\}^2 t_{1i} \\ &\quad + \{a_{11}(a_{i5} + \sqrt{3/2} a_{i4}) - a_{12}(a_{i3} + \sqrt{3/2} a_{i4})\}^2 t_{2i}], \end{aligned} \quad (3.17)$$

and

$$\begin{aligned} ZR &= 2 \sum_{i=3,4,5} [\{a_{11}(-a_{i3} + \sqrt{3/2} a_{i4}) \\ &\quad + a_{12}(a_{i5} - \sqrt{3/2} a_{i4})\}^2 t_{1i} \\ &\quad + \{a_{11}(a_{i5} - \sqrt{3/2} a_{i4}) \\ &\quad + a_{12}(a_{i3} - \sqrt{3/2} a_{i4})\}^2 t_{2i}]. \end{aligned} \quad (3.18)$$

From the simultaneous equations (3.16) with (3.14a), we can obtain $\langle \delta S_x^{(1)} \rangle$ and $\langle \delta S_x^{(2)} \rangle$ separately. The average magnetic moment induced by the external magnetic field being given by $-\mu_0(g_x \langle \delta S_x^{(1)} \rangle + g_y \langle \delta S_x^{(2)} \rangle)/2$, we get the total perpendicular susceptibility including the temperature-independent terms as follows:

$$\chi_{\perp} = \frac{N\mu_0^2 [g_x^2 Q + g_y^2 R + QR\{k\gamma(g_x - g_y)^2 - k\alpha(g_x + g_y)^2\}/2]}{2 + k(\gamma - \alpha)(Q + R) - 2k^2 \alpha \gamma QR} + N\mu_0^2 (A_x + A_y). \quad (3.19)$$

Taking the limit of $\beta \rightarrow \infty$ in (3.17) and (3.18), we get Q and R at the absolute zero of temperature:

$$Q_0 = 2 \left[\frac{\{a_{11}(a_{33} + \sqrt{3/2} a_{34}) + a_{12}(a_{35} + \sqrt{3/2} a_{34})\}^2}{E_1 - E_3} + \frac{\{a_{11}(a_{35} + \sqrt{3/2} a_{34}) - a_{12}(a_{33} + \sqrt{3/2} a_{34})\}^2}{E_2 - E_3} \right], \quad (3.20)$$

$$\begin{aligned} R_0 &= 2 \left[\frac{\{a_{11}(-a_{33} + \sqrt{3/2} a_{34}) + a_{12}(a_{35} - \sqrt{3/2} a_{34})\}^2}{E_1 - E_3} \right. \\ &\quad \left. + \frac{\{a_{11}(a_{35} - \sqrt{3/2} a_{34}) + a_{12}(a_{33} - \sqrt{3/2} a_{34})\}^2}{E_2 - E_3} \right]. \end{aligned}$$

Using (2.10), we have Q and R in the temperature range of $T \geq T_N$:

$$\begin{aligned} Z'Q &= 2\{t_{15} + (\cos \theta - \sqrt{3} \sin \theta)^2 t_{23} + (\sin \theta + \sqrt{3} \cos \theta)^2 t_{24}\}, \\ Z'R &= 2\{t_{25} + (\cos \theta + \sqrt{3} \sin \theta)^2 t_{13} + (\sin \theta - \sqrt{3} \cos \theta)^2 t_{14}\}. \end{aligned} \quad (3.21)$$

which correspond to the results obtained by Moriya et al.

3c) *The effect of the anisotropy on the temperature variation of $\chi_{\perp}$ below T_N*

Using the obtained formula for the perpendicular susceptibility, its temperature variation below the Néel point could be investigated. For this purpose, however, the general expression of $\chi_{\perp}$ is too complicated, so that we assume some approximations and attempt to simplify the formulae relating to $\chi_{\perp}$. Furthermore, for the purpose of investigating the temperature variation below the Néel point, we shall content ourselves with the comparison between the values at the Néel point and the absolute zero. This procedure may be permitted, because $\chi_{\perp}$ seems to be expressed by a monotonous function of temperature.

Let us first derive the approximate expressions for Q and R at T_N . We assume that both D_1 and D_2 are much smaller than kT_N , so that t_{ij} (3.8) can be expanded into powers of $\beta_N D_i$. Omitting higher orders than quadratic of $\beta_N D_i$ in $\exp(-\beta E_i)$ and using (3.21), we get after some calculations Q and R at T_N as

$$Q/2\beta_N = 1 - \frac{7}{20}(2u_1 - u_2) + \frac{21}{20}u_2, \quad (3.22)$$

$$R/2\beta_N = 1 - \frac{7}{20}(2u_1 - u_2) - \frac{21}{20}u_2,$$

where u_i are defined by

$$u_i = \beta_N D_i, \quad i=1, 2. \quad (3.23)$$

The exchange parameter α can also be obtained at the Néel point, as shown by the relation (3.13). In the same method as deriving Q_N and R_N mentioned above, α is written as

$$2k\alpha\beta_N = 1 - \frac{7}{10}(2u_1 - u_2). \quad (3.24)$$

Let us next drive the approximate expressions for Q and R at 0°K . As stated in §3a), the spontaneous magnetization of sublattices at 0°K shrinks from its maximum value 2, thus we can write $\langle S \rangle_0$ as

$$\langle S \rangle_0 = 2(1 - \Delta S). \quad (3.25)$$

Taking account of (3.24), the energies (2.4) at

0°K can be expanded with respect to $D_i/2k\alpha$. Thus we have the approximate energies which are necessary to calculate Q_0 and R_0 (3.20), by omitting higher orders than quadratic of $D_i/2k\alpha$, as follows:

$$\begin{aligned} E_i - A_i &= (-1)^i 2k\alpha(1 - \Delta S)\left(1 + \frac{9}{8}v_2^2\right), \quad i=1, 2, \\ E_3 - A_3 &= -4k\alpha(1 - \Delta S)\left(1 + \frac{3}{8}v_2^2\right), \end{aligned} \quad (3.26)$$

where v_i are defined by

$$v_i = D_i/2k\alpha, \quad i=1, 2. \quad (3.27)$$

In deriving (3.26), we assume tacitly that ΔS should be proportional to v_2^2 . Applying (3.26) to (2.9), the matrix elements a_{ij} and ΔS at 0°K are written as

$$\begin{aligned} a_{12}/a_{11} &= 3v_2/4, \\ a_{32}/a_{33} &= \sqrt{6}v_2/4, \quad a_{35}/a_{33} = 3v_2^2/16, \\ \Delta S &= 3v_2^2/8. \end{aligned} \quad (3.28)$$

Using the derived results and transforming v_i into u_i with the use of (3.24), we get Q and R at 0°K from (3.20):

$$\begin{aligned} Q_0/2\beta_N &= 1 - \frac{4}{5}(2u_1 - u_2) + \frac{3}{2}u_2, \\ R_0/2\beta_N &= 1 - \frac{4}{5}(2u_1 - u_2) - \frac{3}{2}u_2. \end{aligned} \quad (3.29)$$

As the approximate expressions for Q and R have been derived, next we attempt to simplify the formula of $\chi_{\perp}$ (3.19). Defining

$$\begin{aligned} Q_{\perp} &= (Q + R)/2, \quad g_{\perp} = (g_x + g_y)/2, \\ \Delta Q &= Q - R, \quad \Delta g = g_x - g_y. \end{aligned} \quad (3.30)$$

and neglecting the higher orders quadratic of $\Delta Q/Q_{\perp}$, the approximate formula of $\chi_{\perp}$, except for the temperature-independent part, is written as

$$\chi_{\perp}(T) = \chi_{\perp}^m \left\{ 1 + \frac{1 + \xi}{4(1 - k\alpha Q_{\perp})} \left(\frac{1}{1 + \xi} \frac{\Delta Q}{Q_{\perp}} + \frac{\Delta g}{g_{\perp}} \right)^2 \right\}, \quad (3.31)$$

$$\chi_{\perp}^m = N\mu_0^2 g_{\perp}^2 Q_{\perp} / (1 + k\gamma Q_{\perp}), \quad (3.31a)$$

where ξ is the ratio of the exchange parameters defined by (2.2) and (3.2):

$$\xi = \gamma/\alpha. \quad (3.32)$$

Inserting the approximate formulae of Q and R into (3.31), we get the ratio of $\chi_{\perp}(0)$ to $\chi_{\perp}(T_N)$:

$$\frac{\chi_{\perp}(0)}{\chi_{\perp}(T_N)} = 1 - \frac{9}{5(1+\xi)} \frac{u_1(u_1-u_2)}{2u_1-u_2} - \frac{1}{14} \frac{1+\xi}{2u_1-u_2} \left(\frac{4g}{g_{\perp}} \right)^2 \quad (3.33)$$

(3.33) indicates the effect of the anisotropy energy on the temperature variation of $\chi_{\perp}$ and states that both u_1 and u_1-u_2 must be positive in order to explain the experimental fact that $\chi_{\perp}$ below the Néel point decreases with decreasing temperature. In terms of the components of the D -tensor, u_1 and u_1-u_2 are equal to $\beta_N(D_y-D_z)$ and $\beta_N(D_x-D_z)$ respectively, so that the condition stated above is equivalent to say that the z -axis must be the most preferred one of all. One should remark the following points; It is forbidden that $1+\xi$ is negative, otherwise $\chi_{\parallel}$ at T_N becomes negative. In addition, in the rutile type structure, even if either u_1 or u_1-u_2 becomes negative, the spin alignment can be along the z -axis, such as in the case of CoF_2 about which the theoretical investigation was performed by Nakamura and Taketa⁹). However it is unfavourable to the spin alignment that both u_1 and u_1-u_2 are negative.

§ 4. Comparison with Experiment

In order to get the numerical values of the magnetic susceptibility, it is necessary to know the values of D -tensor, g -factor and exchange integral. Tinkham⁷) has obtained experimentally the energy separation between the lowest and the next levels of (1.1a) and g_z by the paramagnetic resonance of Fe ions included in ZnF_2 as impurities. To get the components of D -tensor, he has made the theoretical formula of magnetic anisotropy $\chi_{\parallel}-\chi_{\perp}$ fit the experimental data at various temperatures; obtaining

$$\begin{aligned} D_1 &= 8.06 \text{ cm}^{-1}, & g_z &= 2.24, \\ D_2 &= 1.42 \text{ cm}^{-1}, & g_{\perp} &= 2.04, \end{aligned} \quad (4.1)$$

From (4.1) and the value of T_N , u_1 and u_2 are equal to 0.148 and 0.026 respectively. Therefore the assumptions in §3c) are very good.

The D -tensor stated above consists of the two main contributions: one from the spin-orbit coupling and the other from the spin-spin interaction. To get g_z and g_y (or A_x and A_y) individually, it will be necessary to separate these two contributions. However we do not attempt to do it, because of the fact that $|4g|/g_{\perp}$ is very small as compared with

one, so that $\chi_{\perp}$ is approximately determined only by $g_{\perp}$. The exchange parameter α can be estimated by the relation (3.13), by using the values of D_i and T_N . The exchange parameter γ is so chosen as to make the calculated susceptibilities fit the experimental values.

It is the spontaneous magnetization versus T curve that makes the basis of the numerical evaluations of susceptibilities below T_N . $\langle S \rangle$ is given by the self-consistent equation (3.5). Using (4.1), we get the $\langle S \rangle$ versus T curve which is shown in Fig. 1. Since the magnitude of u_2 is very small, $\langle S \rangle_0$ is very nearly equal to 2. For the comparison we show in Fig. 1 the curve obtained from the Brillouin function of $S=2$. Using the curve (a) of $\langle S \rangle$ and the formulae of susceptibilities,

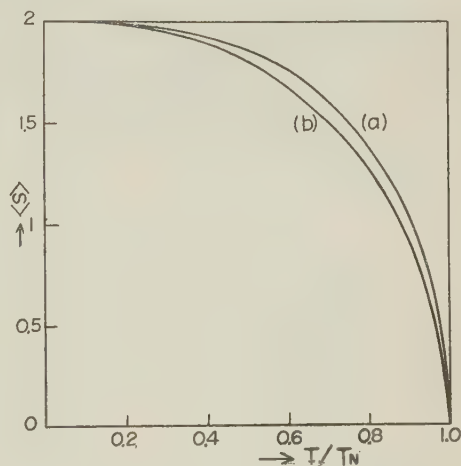


Fig. 1. Curves of $\langle S \rangle$ versus T . Curve (a) is obtained from Eq. (3.5) using the numerical values of D_i by Tinkham and (b) from the Brillouin function of $S=2$.

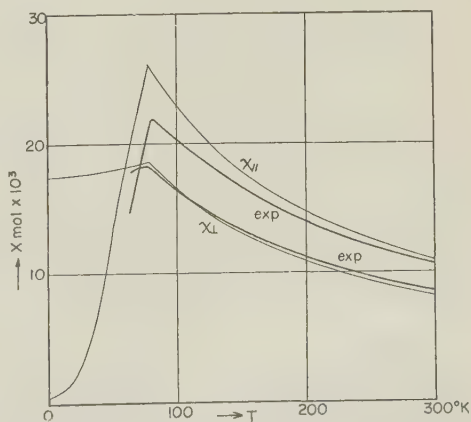


Fig. 2. Curves of $\chi_{\parallel}$ and $\chi_{\perp}$ versus T .

we have the numerical values of $\chi_{\parallel}$ and $\chi_{\perp}$ which are shown in Fig. 2 together with the experimental values²⁾, where the exchange parameter $k\alpha$ is equal to 22.9 cm^{-1} and γ is chosen as 1.24α . The temperature-independent parts of the magnetic susceptibilities are added by assuming the spin-orbit coupling constant to be a free ion value -100 cm^{-1} . $\chi_{\perp}$ below $T_{\perp}$ decreases with decreasing temperature, displaying the same behaviour as the experimental one. The ratio of $\chi_{\perp}$ at 0°K to that at T_N is equal to 0.943, the value of $\chi_{\perp}$ at 0°K being 17.5×10^{-3} . As stated in §1, the experimental value of this ratio is about 0.9, but it should be remarked that this value was obtained by the extrapolation based on the assumption that $\chi_{\parallel}$ approaches zero at 0°K . $\chi_{\parallel}$ at 0°K has the non-zero value which arises from both P_0 (3.11) and the temperature-independent part. However the former gives only a little contribution because of the small u_2 , so that $\chi_{\parallel}$ at 0°K is equal to 0.6×10^{-3} from the value of g_z . In Fig. 3 we compare the calculated $\chi_{\parallel} - \chi_{\perp}$ with the experimental one.²⁾

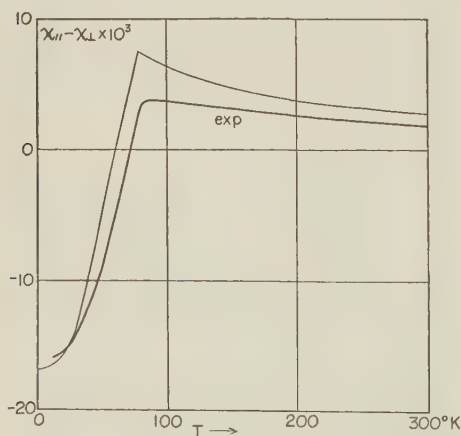


Fig. 3. Curves of $\chi_{\parallel} - \chi_{\perp}$ versus T .

If we take into account that the molecular field approximation is used and hence the good predictions of the magnetic behaviour near the Néel point could not be expected, the agreement of calculated susceptibilities with the experimental ones seems to be good.

§ 5. Summary

By the molecular field approximation, the magnetic susceptibility of FeF_2 was studied. In particular we investigated in some detail

the effect of the anisotropy energy on the temperature variation of $\chi_{\perp}$ below the Néel point and obtained the condition which is necessary to explain the experimental fact that $\chi_{\perp}$ decreases with decreasing temperature. This condition says that both D_1 and $D_1 - D_2$ must be positive, meaning that the z -axis is the most preferred one of the $1, 1$ under the assumptions that both D_1 and D_2 are much smaller than kT_N and the higher orders of $4Q/Q_{\perp}$ can be omitted. According to the experimental data by Tinkham, these assumptions are valid. In FeF_2 , therefore, the symmetry of the anisotropy energy is essentially equivalent to the tetragonal one and is remarkably different from the one in CoF_2 ⁹⁾.

The numerical evaluations were performed by using Tinkham's data and $\gamma/\alpha = 1.24$, and we found that the calculated susceptibilities seem to be in good agreement with the experimental values if we take account of the fact that Tinkham's data were obtained about Fe ions which are included in ZnF_2 as impurities. The temperature variation of the calculated perpendicular susceptibility below the Néel point shows the same behaviour as the experimental one; obtaining the ratio of $\chi_{\perp}$ at 0°K to that at T_N to be 0.943 which is compared with the experimental value of about 0.9. This value, however, was obtained by the extrapolation with the use of powder data as stated in §1, so that the more accurate measurements for single crystals are desirable. At the absolute zero of temperature, as u_2 is very small, the spontaneous magnetization of sublattices is almost equal to 2. Therefore P_0 , which arises from the fact that the magnetic field parallel to the z -axis induces the virtual transitions and hence is proportional to u_2^2 , contributes little to $\chi_{\parallel}$.

Finally we shall refer to the temperature dependence of magnetic anisotropy at very low temperatures. The experimental fact states that it is proportional to T^4 at hydrogen temperatures. The molecular field approximation can not predict this behaviour. According to the spin wave theory by Eisele and Keffer¹⁰⁾, $\chi_{\parallel}$ is given by

$$\chi_{\parallel} = C \sum_{n=1}^{\infty} K_2(nT_{AB}/T).$$

Here K_2 is the real Hankel function of degree 2 and T_{AB} in our case is defined by

$$kT_{AB} = \sqrt{2S\{2Z_2J_2(2D_1 - D_2) + 2D_1(D_1 - D_2)\}^{1/2}},$$

and C is a factor independent of temperature. The temperature variation of magnetic anisotropy at low temperatures seems to be governed by that of $\chi_{\parallel}$. Therefore we shall investigate K_2 as a function of T^4 . One sees that this function has a point of inflexion at $x_I = T_{AB}/T_I = 3.9$ besides zero and infinity, and above and below x_I , K_2 is convex and concave respectively towards the T^4 -axis. We make the tangent at x_0 and regard it as an approximate value of the original function. If we choose, for instance, x_0 as 5.3, the range of x over which the errors in doing so lie within 10% is from 3.9 to 6. Therefore if the appropriate value of T_{AB} is chosen, the experimental behaviour could be explained. Using the numerical values in §4, T_{AB} becomes 89.5°K.

The author would like to express his deep thanks to Dr. T. Oguchi for suggesting this study as well as his helpful advice and to Professor M. Toda for his kind interest and

valuable suggestion. He also wishes to thank Dr. M. Shimizu of the Tokyo Metropolitan University for valuable discussion.

References

- 1) J. W. Stout and Ě. Catalano: J. Chem. Phys. **23** (1955) 1803, 2013.
- 2) J. W. Stout and L. M. Matarrese: Revs. Mod. Phys. **25** (1953) 339.
- 3) H. Bizette and B. Tsai: Compt. rend. **212** (1941) 119.
- 4) K. Niira and T. Oguchi: Progr. Theor. Phys. **11** (1954) 425.
- 5) T. Moriya, K. Motizuki, J. Kanamori and T. Nagamiya: J. Phys. Soc. Japan **11** (1956) 211.
- 6) A. Abragam and M. H. L. Pryce: Proc. Roy. Soc. A, **205** (1951) 135.
- 7) M. Tinkham: Proc. Roy. Soc. A, **236** (1956) 535, 549.
- 8) R. A. Erickson: Phys. Rev. **90** (1953) 779.
- 9) T. Nakamura and H. Taketa: Progr. Theor. Phys. **13** (1955) 129.
- 10) J. A. Eisele and F. Keffer: Phys. Rev. **96** (1954) 929.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 3, MARCH, 1960

Volume Magnetostriction of Cobalt-nickel Alloys

By Takejiro KANEKO

*The Research Institute for Iron, Steel and Other Metals,
Tohoku University, Sendai, Japan*

(Received October 22, 1959)

Forced volume magnetostriction of cobalt-nickel alloys with 10, 20 and 30 atomic percent nickel content was measured by means of resistance strain-gauge up to the magnetic field of 15000 Oe. It was observed that the fractional volume change per oersted of these alloys after technical saturation were smaller than $1 \times 10^{-10}/\text{Oe}$. The result is consistent, at least qualitatively, with Patrick's experimental results of the change of the Curie temperature with hydrostatic pressure.

§ 1. Introduction

The volume magnetostriction of the primary solid solution alloys with h.c.p. structure in cobalt-nickel system was investigated once by Mashiyama¹⁾ and the fractional changes of volume due to magnetization, $\partial\omega/\partial H$ ($\omega = \Delta V/V$, V : volume, ΔV : volume change, H : magnetic field), were found to be comparatively large, viz. 15×10^{-10} Oe. However,

since the maximum magnetic field strength used by this author was about 1500 Oe, his results for h.c.p. alloys should be interpreted as being contaminated with magnetostriction which took place before technical saturation had been reached. Therefore, we performed the measurements of volume magnetostriction of cobalt-nickel alloys in magnetic fields strong enough to rule out any ambiguity

arising from incomplete saturation of the specimens.

§ 2. Specimens and Experimental Procedure

Three cobalt-nickel alloys, containing 10, 20 and 30 atomic percent nickel, were melted by means of a vacuum induction furnace, cast in a metal mould 20 mm in diameter, forged and then machined into rectangular parallelepipeds measuring $10 \times 10 \times 20 \text{ mm}^3$. They were then heated in the vacuum furnace at 950°C for about 7 hours and cooled slowly. Then the specimens were examined by means of the X-ray analysis technique. It was confirmed by the Debye-Scherrer method that alloys containing 10 and 20% nickel were in the range with h.c.p. structure, while 30% nickel alloy was a mixture of h.c.p. and f.c.c. phases.

The measurements of magnetostriction were performed by means of resistance-strain gauge. Resistance-strain gauges were stuck to the surface of the specimen both in the longitudinal and transverse directions of the rectangular parallelepiped. The specimens were placed between the pole pieces of an electromagnet (spindle diameter: 7 cm), the longer side of the parallelepiped being parallel to the direction of the magnetic field. The longitudinal and transverse magnetostrictions were measured independently and the volume magnetostriction was derived by using the relation

$$\frac{\Delta V}{V} = \frac{\Delta l}{l} + 2 \frac{\Delta t}{t}, \quad (1)$$

where $\Delta l/l$ and $\Delta t/t$ are the fractional changes in the longitudinal and transverse directions of the specimens respectively. Now, a thermal expansion due to the magneto-caloric effect will occur during magnetization, which

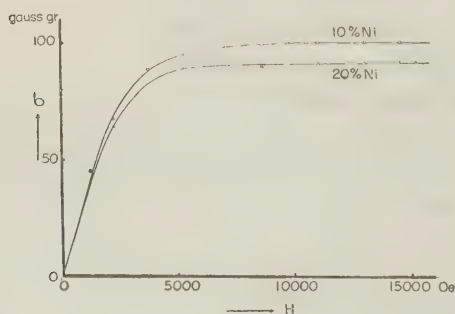


Fig. 1. The curves of specific magnetization versus magnetic field.

will disturb the measurement. As a matter of fact, however, the error from this source did not exceed $6 \times 10^{-12}/\text{Oe}$,* which was far less than the observed value of magnetostriction. The specimen was also placed in a copper vessel with large heat capacity, the surfaces of the specimen being kept in close contact with the vessel so that the heat produced in the specimen by magnetocaloric effect could be readily taken away by heat conduction.

§ 3. Result and Discussion

First the magnetization curves were taken of the specimens with the nickel concentration of 10 and 20%. (Fig. 1.) It was considered that saturation magnetization was reached at magnetic field strength of the order of 8000 Oe.

The results of measurements of the magnetostriction in the longitudinal and the transverse directions are shown in Figs. 2 and 3.

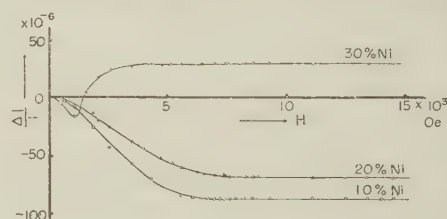


Fig. 2. The curves of longitudinal magnetostriction versus magnetic field.

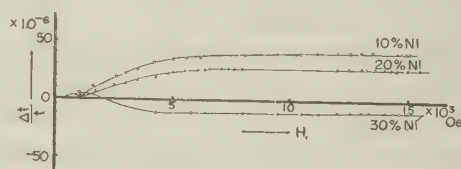


Fig. 3. The curves of transverse magnetostriction versus magnetic field.

* Temperature rise of a specimen by magnetocaloric effect ΔT is

$$\Delta T = \frac{T}{C_H} \left(\frac{\partial I}{\partial T} \right)_H \Delta H$$

in which T is the temperature, I the magnetization and C_H the specific heat. Adiabatic volume change by the effect per Oersted $(\partial \omega / \partial H)_{\text{ad}}$ is

$$\left(\frac{\partial \omega}{\partial H} \right)_{\text{ad}} = -3\alpha \frac{\Delta T}{\Delta H} = -\frac{3dT}{C_H} \left(\frac{\partial I}{\partial T} \right)_H$$

(α : linear thermal expansion coefficient). Putting appropriate values for T , C_H , $\partial I / \partial T$ and α in the above equation, the value of $(\alpha \omega / \alpha H)_{\text{ad}}$ is calculated to be about 6×10^{-12} per Oe.

The accuracy of these measurements is in the order of 1×10^{-6} .

Using the above results, we obtained the volume magnetostrictions, and their results are shown in Fig. 4. As can be seen in it, the volume magnetostrictions for these cobalt-nickel alloys appeared to have linearity in magnetic fields above 10000 Oe. We may deduce the forced magnetostriction constants from the slope of the curve in high fields.

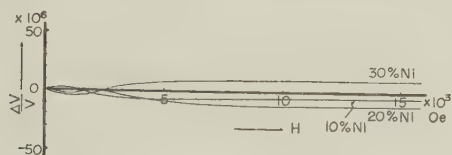


Fig. 4. The volume magnetostriction deduced from longitudinal and transverse versus magnetic field.

It was found that the fractional change of the volume magnetostriction with the magnetic field $\partial\omega/\partial H$ was smaller than 1×10^{-10} Oe within the accuracy of our measurements, and was far smaller than that due to Mashiyama mentioned above. The results by Mashiyama may be considered to correspond to the magnetostriction in the rotation range of magnetization.

Now, if the specific magnetization and the Curie temperature of the specimen are denoted by σ and θ respectively, and if σ_0 , the specific magnetization at absolute zero, is assumed to be independent of pressure, then the fractional change³⁾ of the Curie point by hydrostatic pressure is given by

$$\frac{1}{\theta} \cdot \frac{\partial\theta}{\partial P} = \frac{\partial\omega/\partial H}{T(\partial\sigma/\partial T) - 3(\alpha/\kappa)(\partial\omega/\partial H)}, \quad (2)$$

in which α is the linear thermal expansion coefficient and κ the volume compressibility. In equation (2), the second term in the denominator is negligibly small as compared with the first. And since $T(\partial I/\partial T)$ is always negative, it is derived from equation (2) the fractional change of the Curie point with pressure $1/\theta \cdot \partial\theta/\partial P$ has the sign opposite with that of forced volume magnetostriction $\partial\omega/\partial H$. By putting the observed values of forced volume magnetostriction in equation (2), the change in the Curie point due to hydrostatic pressure $\partial\theta/\partial P$ is found to be less than 10^{-3} deg/atm for these alloys. Indeed, the investigation of Patrick³⁾ indicates that $\partial\theta/\partial P$ for nickel and cobalt is $(0.35 \pm 0.02) \times 10^{-3}$ and $(0 \pm 1) \times 10^{-3}$ deg/atm respectively. The value of the changes in the Curie point by hydrostatic pressure for cobalt-nickel alloys, mentioned above has a same order of magnitude with them of nickel and cobalt.

Acknowledgements

The author wishes to express his cordial thanks to Profs. T. Hirone, S. Maeda, S. Nagasaki and H. Watanabe for their kind guidance in his studies of the present project. Also he wishes to express his hearty thanks to Mr. I. Maekawa for his assistance in the experiments.

References

- 1) Y. Mashiyama: Sci. Rep. Tohoku Univ. **22** (1933) 338,
- 2) L. Kornetzki: Z. Phys. **98** (1938) 289.
- 3) L. Patrick: Phys. Rev. **93** (1954) 384.

Magnetic Anisotropy Measurement of MnO Single Crystal

By Enji UCHIDA, Hisamoto KONDOH

Department of Physics, University of Osaka Prefecture

Yoshihide NAKAZUMI

Tochigi Chemical Industry Co., Ltd., Osaka

Takeo NAGAMIYA

Department of Physics, Osaka University

(Received November 2, 1959)

The magnetic anisotropy of MnO single crystal, grown by the Verneuil method, was measured using a torque balance. The results of the torque measurements at liquid air temperature could be summarized within experimental errors by a formula

$$T = C_1 H^2 \sin(2\theta + \varepsilon_1) + C_2 H^4 \sin(4\theta + \varepsilon_2) + C_3 H^6,$$

where H is the applied field intensity, θ the angle of rotation of H relative to the crystal, and ε 's and C 's are constants which depend in a certain way on the kind of crystallographic axis of suspension. In the case where $[111]$ is the direction of suspension, $C_2 = 0$. The $C_3 H^6$ term changed its sign when the rotation was made in the reverse sense; thus it represents a rotational hysteresis term. Alternative theoretical interpretations of the new 4θ -term are presented: it arises either from a possible small anisotropy energy within the easy plane of magnetization, or from reversible movements of the walls which separate different antiferromagnetic domains. Discussion to favor the latter is given.

§ 1. Introduction

Manganese monoxide is well known^{(1),(2)} to be an antiferromagnetic crystal with a Néel point at 116°–118°K. It is also known⁽¹⁾ that its susceptibility shows a field-dependence below the Néel temperature. Its magnetic structure has been studied by neutron diffraction experiment first by Shull et al.⁽³⁾ and more recently by Roth⁽⁴⁾. The latter author determined a structure in which the plus and minus spins occupy alternately (111) planes and the spin axis is confined in this plane. (From symmetry consideration, possible easy axes may be either $[\bar{1}10]$, $[0\bar{1}1]$ and $[10\bar{1}]$ or $[11\bar{2}]$, $[\bar{2}11]$ and $[1\bar{2}1]$.) Roth's structure conforms to the theoretical considerations developed by the following several investigators. Kaplan⁽⁵⁾ inferred, by calculating the magnetic dipolar interaction energy, that (111) would be the easy plane of magnetization. Keffer and O'Sullivan⁽⁶⁾ showed that, if one

takes only dipolar interaction into account, the relative orientations of the spin axes of the four sublattices (corresponding to the f.c.c. arrangement of Mn^{++}) cannot uniquely be determined; they suggested, however, that the small rhombohedral distortion of the lattice, observed by X-rays by Rooksby⁽⁷⁾, would make (111) the easy plane of magnetization. More recently, Nagamiya⁽⁸⁾ has shown that the small rhombohedral distortion actually imposes a further restriction to the spin axes and confines them in the (111) plane. He considered the decrease in exchange energy due to this distortion and showed that this decrease is equal to twice the increase in elastic energy due to the same distortion. Minimizing the sum of the exchange energy and dipolar energy, he showed that the spin axis is uniquely determined and is stabilized in the (111) plane.

The present experiment was carried out, as an extension of our previous experiment on NiO ⁽⁹⁾, to see what the anisotropic character of the MnO single crystal is. We have found that the torque exerted on the crystal by the magnetic field consisted of Fourier terms of periods 180° and 90° of the angle of rotation

* The authors have taken parts as follows:
Y. Nakazumi: Preparation of single crystals and X-ray study, E. Uchida and H. Kondoh: Magnetic torque measurements, T. Nagamiya: Theoretical analysis.

of the magnetic field and a small constant term which changed its sign when the rotation was made in the reverse way. The 90° term, which was not observed in the case of NiO, will be interpreted in §4 and §5 to be due either to the anisotropy energy within the $\{111\}$ plane or to the movements of the anti-ferromagnetic domain walls.

§ 2. Experimental

Single crystals of MnO were grown by the flame fusion method of Verneuil, the flame having been finely controlled so as to have an excess composition of hydrogen⁽¹⁰⁾. Referring to thermal analysis data obtained by us of the manganese-oxygen system, we found it preferable first to prepare powder MnO of high purity by heating powder MnO₂ (99.9% pure) at about 700°C for one day in H₂ atmosphere. By melting this powder in the flame, single crystals were grown. A boule of crystal taken out from the furnace had a bullet-like shape, about 1 cm in diameter and a few cm long (see Fig. 1). The room temperature Laue back reflection X-ray picture or rotation photograph showed that the crystal was a good single crystal (see Fig. 2); in most specimens we scarcely found any traces

of higher oxides (e.g. Mn₃O₄). The lattice constant, $a=4.445\text{\AA}$ (at room temperature), calculated from these patterns conforms very well to that given by Wyckoff⁽¹¹⁾ or by N.B.S.⁽¹⁴⁾

The crystal can be cleaved along $\{100\}$ to a rectangular parallelepiped. By cleaving and grinding we prepared samples of the shape shown in Fig. 3; a parallelepiped of a few mm in edge lengths was ground in such a way that $\{111\}$ or $\{\bar{1}\bar{2}1\}$ planes appear at the corners and $\{110\}$ or $\{1\bar{1}0\}$ at the edges of it. This shape is convenient for the purpose of exactly mounting the sample with desired crystal orientations. Misorientations of the ground-out surfaces are within 3° , when judged from the precision of our grinding apparatus.

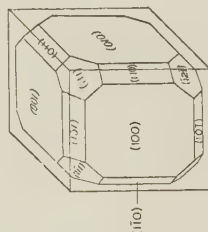


Fig. 3. Made-out shape of the sample. The cube represents the original cleven-out sample.

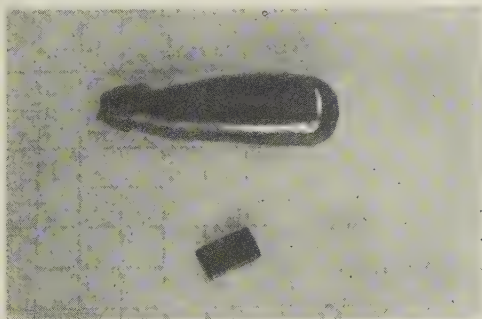


Fig. 1. A boule of MnO single crystal grown by the Verneuil method and a cleven-out crystal.

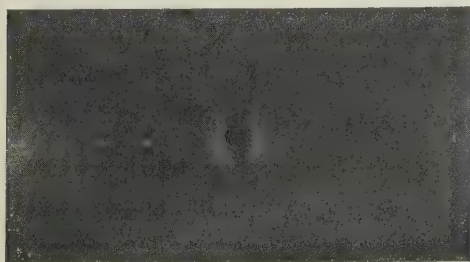


Fig. 2. Rotation photograph of a MnO single crystal, No. 415, taken by a perpendicular incidence of Fe K α radiation at room temperature.

Magnetic torque measurements were made by using a torsion balance. Since the details of our equipments and method of measurements are almost the same as those in our previous experiment on NiO single crystal⁽⁹⁾, they will not be reported here, except that the following device was made in the present case in order to improve accuracy in the measurements. A horizontal magnet, whose pole pieces have flat surfaces of 12 cm in diameter, is allowed to rotate about a vertical axis, and the crystal is freely hung along this axis of rotation. (Previously, the magnet was fixed and the crystal was rotated.) The angular direction of the magnet can be read to within 0.2° . The magnitude of the torque acting on the sample is measured by reading the rotation of the torsion head which is required to make the sample rest at its normal position, i.e., the position for zero field; this procedure was convenient to keep the sample free from any 'rotational hysteresis' which will be mentioned in the next paragraph. The normal position was checked by observa-

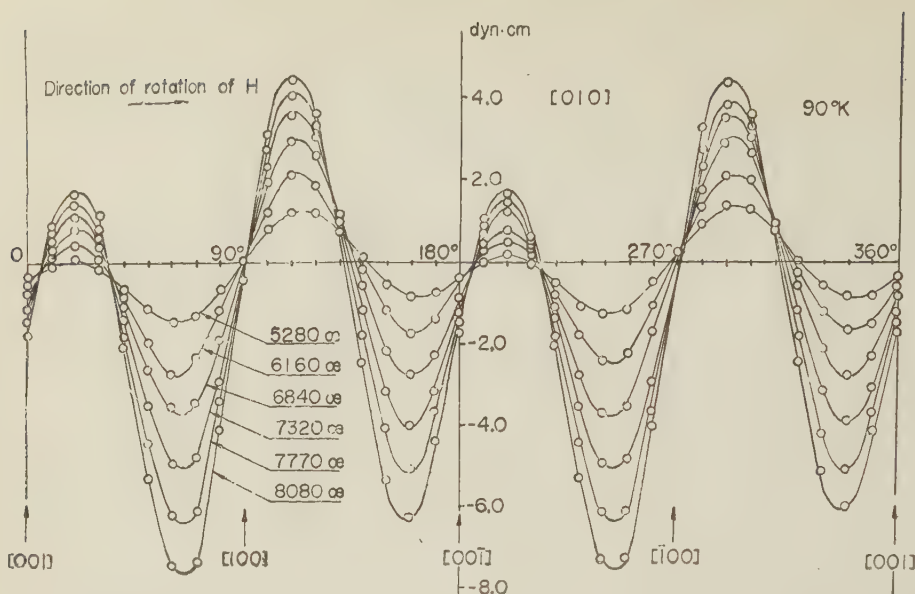


Fig. 4. Magnetic torque curves obtained with a MnO single crystal, No. 415, when the axis of suspension is $[010]$; 90°K . Arrows indicate position where the respective crystallographic axes coincide with the direction of the magnetic field.

tion with a telescope. The torsion fibre is a ribbon wire of phosphor bronze, 1 mm wide and 0.03 mm thick. With a suspension ribbon of a length of 12 cm, the torsion constant was 7.46×10^{-2} dyn cm deg^{-1} . Since MnO has a Néel temperature at about 116°K , the torque measurements have been done mostly at liquid oxygen temperature (90°K).

§ 3. Results

In the present experiment, it was observed that the torque was always accompanied with a hysteresis, i.e., the torque did not take the same values when the rotation of the applied field was reversed; the observed torque curve was not stationary in the starting stage of each run and it was only after rotating the applied magnetic field by about 180° in one direction that the torque values became stationary and reproducible. In Fig. 4 are shown the stationary torque curves versus the angle of rotation of the magnet, in the case where the sample was suspended along its $[010]$ axis and in the range of field up to 8080 oe. Each curve in this figure contains two sinusoidal components, one with a period of 180° and the other with a period of 90° , and furthermore a constant component. This decomposition for the case $H=8080$ oe is shown in Fig. 5. By analysing all the observed torque curves into such three components, it was

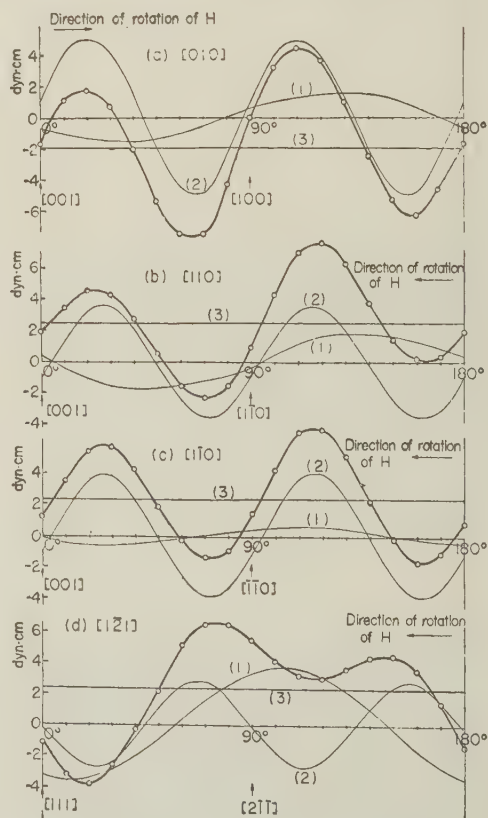


Fig. 5. Magnetic torque curves (thick curves) obtained with a MnO single crystal, No. 415, when the axis of suspension is a) $[010]$, b) $[110]$, c) $[1\bar{1}0]$, d) $[1\bar{1}2]$, and their Fourier components (thin curves); 1) with 180° period, 2) with 90° period and 3) a constant term.

found that the amplitude of the component with period 180° was closely proportional to H^2 over the range 5280 oe to 8080 oe, while the amplitude of the component with period 90° was even more strictly proportional to H^4 in the same range. The constant term increased more rapidly with increasing field and was roughly proportional to H^6 . These results are shown in Fig. 6.

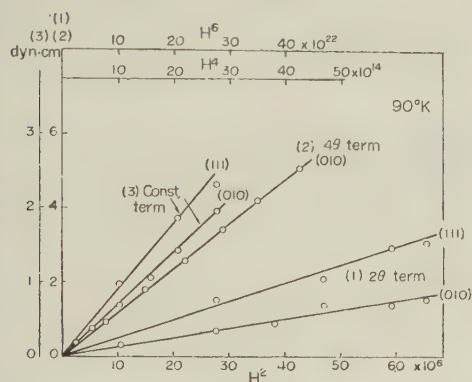


Fig. 6. Field dependence of the amplitudes of torque components for MnO single crystal, No. 415, 1) 2θ -term, 2) 4θ -term, 3) constant term plotted against H^2 , H^4 , and H^6 , respectively; 90°K .

Similar results were obtained when the sample was suspended along other crystallographic directions than $[010]$, except when it was suspended along $[111]$, in which case the 90° component vanished as shown in Fig. 7. Therefore, our results for the torque per unit mass, T , can be summarized within experimental errors by a formula

$$T = C_1 H^2 \sin(2\theta + \varepsilon_1) + C_2 H^2 \sin(4\theta + \varepsilon_2) + C_3 H^6, \quad (1)$$

where H is the applied field intensity, ε 's are phase constants, and C 's are amplitude constants. In the case where $[111]$ is the direction of suspension, $C_2 = 0$.

Noteworthy features of our observation were as follows. The amplitude per unit mass and the phase constant of the 2θ -term for a specified axis of suspension varied with thermal or mechanical treatment (cooling by liquid air and re-heating to room temperature, or polishing). Contrary to this, the corresponding quantities of the 4θ -term remained the same and they were characteristic of each specified axis. In our previous experiment on NiO single crystals a similar result was found for the 2θ -term (there was no 4θ -term).

In the case of NiO, the single crystal was composed of small rhombohedral crystallographic domains twinned through $\{100\}$ planes, as we actually examined them by X-rays. The distribution of these domains depended on the direction of the crystal growth in the Verneuil furnace; a crystal whose direction of growth was along $[111]$ showed an equal distribution of domains with respect to the three cubic axes, resulting in zero torque when it was suspended along $[111]$, while crystals grown in any other directions had unequal distributions and gave rise to finite torques even in the (111) plane.

Similar behaviors is expected for MnO. No determination of the twin structure has been undertaken, however, since X-ray works had

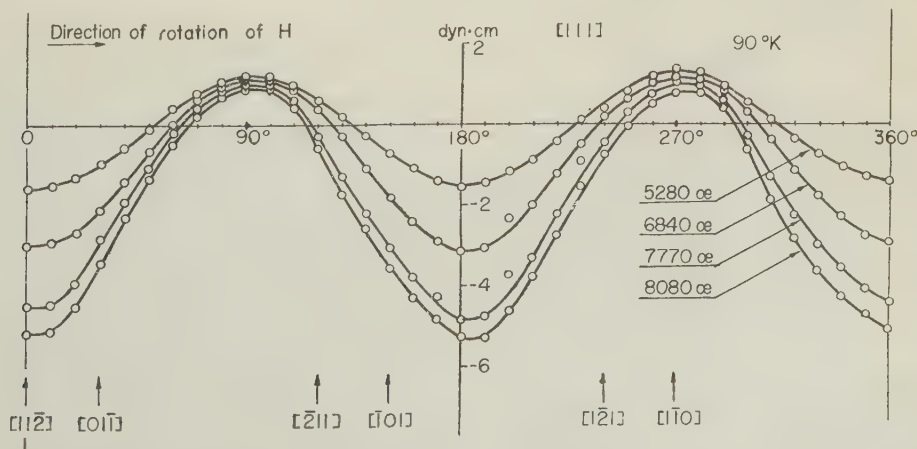


Fig. 7. Magnetic torque curves obtained with a MnO single crystal, No. 415, when the axis of suspension is $[111]$.

to be done at low temperatures. Neither did we apply any technique of aligning domains in the present experiment. The quantity, p , which represents the excess fraction of aligned domains, could be estimated in the present case, as in NiO, from the amplitude of the 2θ -term. It was found that p was of the order of one percent in all the samples of MnO used. This is very small compared with that previously found for those NiO single crystals which were annealed without applying any pressure.

The appearance of the 4θ -term is the most important result in the present experiment. This torque component remains practically unchanged by any thermal or mechanical treatment. From the torque curves, such as those in Fig. 4, (or Fig. 5), the amplitudes of this component per unit mass and their ratios, as well as the phase angle, ϵ_2 , have been calculated and they are listed in Table I. We shall theoretically interpret them in the next section.

Two interesting characteristics are found

Table I. Torque measurements on MnO at liquid air temperature, 90°K, and H=8080 oe. Axis of suspension of the crystal and the corresponding torque amplitude, relative amplitude and phase angle for the 90° term are shown. Constant torque term is also included. Phase angle is measured as mentioned in the text.

Axis of suspension	Amplitude dyn·cm/g	Relative amplitude		Phase angle		Constant term dyn·cm/g
		(exp.)	(theor.)	(exp.)	(theor.)	
mean						mean
[100]	5.36					
[010]	5.66	5.56	1.00	1.00	0±3°	0
[001]	5.66					1.25
[110]	4.16	4.33	0.78	0.75	0±4°	0
[101]	4.11					
[011]	4.45					
[110]	4.16					
[101]	4.11	4.41				
[011]	4.45					
[110]	4.16					
[101]	4.11					
[011]	4.45					
[110]	4.50					
[011]	4.67					
[101]	4.07					
[121]	3.13					
[121]	3.13	3.24	0.58 ₅	0.58 ₃ *	180±2°	180°
[121]	3.26					
[122]	3.43					
{111}	0	0	0	0	—	—

* 0.58₃=7/12

for the third component of the torque, i.e., the constant term. 1) As was mentioned already, the stationary state was attained only after rotating the applied magnetic field in the same sense beyond about 180°. This indicates a rotational hysteresis. By reversing the rotation, it was found that the sign of the constant term in the stationary state reversed its sign. 2) Comparison between the magnitudes of the constant term in different samples showed that it depended strongly on the degree of stoichiometry of the sample. We used samples made out of

three different mother crystals which were numbered as 407, 415 and 426. The crystal of No. 426 is such that the X-ray patterns obtained by it showed the best stoichiometry and the appearance of its cleavage surfaces were the finest. No. 415 comes closely next to this, and No. 407 showed, though very weakly, an extra pattern which corresponded to Mn₃O₄. The crystals of No. 426 showed the largest constant torque, No. 415 a smaller value of it, while those of No. 407 showed scarcely any constant torque (see Table II). These results indicate that the more perfect

the crystal is, the easier is the irreversible rotation of the magnetization of each domain or irreversible movements of the domain walls. A similar example of the constant torque has been reported recently by Chikazumi⁽¹³⁾ in his magnetic torque measurements on thin Ni films.

Table II. Observed value of K_1 and that of constant torque, showing their variation for different samples. The size dimension of their mother crystals and the mass of the made-out samples are listed together.

Sample	Size dimension (mm ³)	Mass (gr)	K_1 erg/gr	Const. comp. dyn cm/gr
No. 407	9×7.5×7	1.644	1.75×10^4	≈0
No. 415	7×5.5×4.5	0.871	1.09×10^4	1.33
No. 426	8×5.8×3.5	0.676	$0.69_2 \times 10^4$	5.62

H=8080 oe

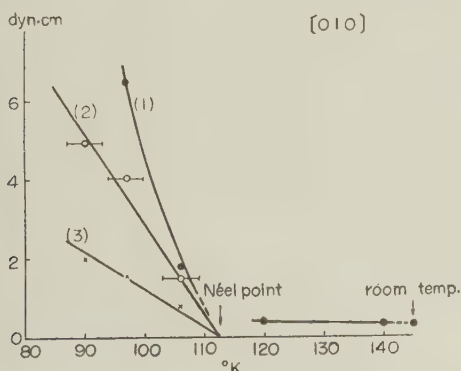


Fig. 8. Temperature dependence of the amplitude of the torque components for a MnO single crystal, No. 415; 1) 2θ -term, 2) 4θ -term, 3) constant term; H=8080 oe. The suspension axis is [010].

Fig. 8 shows the temperature dependence of the torque amplitudes of the 2θ and 4θ -components and of the constant component for the suspension along the axis [010]. The Néel temperature estimated from the vanishing of these components is 113°K. It is noted, however, that a small finite torque was always observed even when the temperature was raised beyond the Néel temperature. This small torque is sinusoidal with period 180° and had a quite different characteristic from the torque component with period 180° observed below the Néel temperature: the former remained unchanged after cooling the sample below the Néel temperature and reheating it, while the latter changed every

time the sample was cooled; this happened in all the samples used in the present experiment. It is believed that this torque originates from a paramagnetic higher oxide of manganese contained in the crystal to a very small amount as an impurity but not from MnO itself.

Effect of field cooling on the torque variation were also studied in the present experiment. It was found that when a sample was cooled down to 90°K from room temperature in the presence of a magnetic field (8080 oe), a significant change was observed in the phase constant of the component of period 180°, in such a way that the position of stable equilibrium became perpendicular to the direction of the field applied during the cooling. The component of period 90° remained without being affected by the field cooling.

§ 4. Interpretation of the Results, I.*

Our experimental results may be interpreted in alternative ways: either the torque component of period 90° is due to the anisotropy energy within the plane of easy magnetization, i.e. (111), or it is due to the movements of walls which separate domains with different directions of magnetization. The former possibility will be discussed in this section and the latter possibility in the next section.

If a single magnetic domain has a spin axis whose direction cosines are α, β, γ and if we apply a magnetic field whose direction cosines are a, b, c , the free energy per unit volume due to the interaction with the applied field will be written as

$$F = -\frac{1}{2}\chi_{\parallel} H_{\parallel}^2 - \frac{1}{2}\chi_{\perp} H_{\perp}^2 \\ = \frac{1}{2}(\chi_{\perp} - \chi_{\parallel})H^2(\alpha a + \beta b + \gamma c)^2 - \frac{1}{2}\chi_{\perp} H^2, \quad (2)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the susceptibilities parallel and perpendicular to the spin axis. We assume that the spin axis is confined in the (111) plane, in virtue of the classical dipolar interaction, and that it is subject to an anisotropy energy of six-fold symmetry in this

* The main part of this and next sections was reported by Nagamiya in his paper "State of Atoms in Magnetic Crystals" which was presented at the Second Welch Foundation Conference in Houston, Texas, December 1958

plane, the easy axes being either $\langle \bar{1}10 \rangle$ or $\langle 11\bar{2} \rangle$. For an applied magnetic field which is low enough to make the spin axis deviate only little from the equilibrium direction, the total anisotropy energy can be written in the form

$$K_1\beta^2 + K_2\gamma^2, \quad (3)$$

where we take the z -axis perpendicular to the (111) plane, the x -axis along the easy axis, and the y -axis perpendicular to the both. K_1 is associated with the anisotropy energy within the plane and K_2 with that which confines the spin axis to the plane; both are functions of temperature. We assume that K_1 is much smaller than K_2 . Adding (3) to (2) and looking for the minimum of the total free energy, the following expression in powers of H^2 can be obtained for the minimum of the total free energy:

$$F = -\frac{1}{2}\chi_{\perp}H^2 + \frac{1}{2}(\chi_{\perp} - \chi_{\parallel})H^2a^2 - \frac{1}{4}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{a^2b^2}{K_1} + \frac{a^2c^2}{K_2}\right) + \dots \quad (4)$$

In order to simplify the matter, we average (4) by applying all the symmetry operations of the original cube, and at the same time transform the coordinate system into such that the x, y, z -axes are the principal axes of the cube. Then we have, up to terms of order H^4 ,

$$F = -\frac{1}{36}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{1}{2K_1} - \frac{2}{K_2}\right)(a^2b^2 + b^2c^2 + c^2a^2) - \frac{1}{6}(2\chi_{\perp} + \chi_{\parallel})H^2 - \frac{1}{36}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{1}{2K_1} + \frac{1}{K_2}\right). \quad (5)$$

The first term in this expression depends on the direction of the applied field and so it gives rise to a torque. The torque can be obtained by differentiating this term with respect to the angle of rotation of the field. Since this expression is quartic with respect to the direction cosines of the applied field relative to the cubic axes, the torque must change sinusoidally with a period of 90° for any axis of suspension. Also, its magnitude must be proportional to H^4 . The theoretical formulae thus obtained for the torque for different crystallographic directions of suspension are as follows:

$$\begin{aligned} \langle 001 \rangle & \quad \frac{1}{72}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{1}{2K_1} - \frac{2}{K_2}\right)\sin 4\theta \\ \langle 110 \rangle \} & \quad \frac{1}{96}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{1}{2K_1} - \frac{2}{K_2}\right)\sin 4\theta \\ \langle \bar{1}10 \rangle \} & \\ \langle 111 \rangle & \quad \text{zero} \\ \langle 1\bar{1}2 \rangle & \quad -\frac{7}{864}(\chi_{\perp} - \chi_{\parallel})^2H^4\left(\frac{1}{2K_1} - \frac{2}{K_2}\right)\sin 4\theta. \end{aligned} \quad (6)$$

In these formulae, the angle, θ , is measured from a cubic principal axis in the plane of rotation for the first three cases and from [111] for the fifth case.

To compare with theory, the experimental results must be averaged by the same cubic symmetry operations. An ambiguity arises in doing so, as each time when we choose a particular crystalline axis as the axis of suspension, the specimen is pulled out from a low temperature region to the room temperature region in order to re-set. During this process the twin structure may change. If this happens, other terms of the free energy which average out to zero by cubic symmetry operations will also contribute to the torque. However, the comparison given in Table I seems to show that there is actually little fear of this change, as there is a complete agreement between theory and experiment.

The anisotropy constant K_1 can be calculated by comparing the absolute magnitude of the measured torque (Table I) and the corresponding theoretical formulae (6). Since K_2 is much larger than K_1 , as will be shown below, the K_2^{-1} term in these formulae can be neglected. Making use of the values of the powder susceptibility obtained by Bizette, Squire and Tsai⁽²⁾ ($\chi_{\parallel} = 41 \times 10^{-6}$ e.m.u./g at $90^\circ K$ and $\chi_{\perp} = 86 \times 10^{-6}$ e.m.u./g), the value of K_1 can be obtained to be 1.09×10^4 erg/g for the sample of the Table I (No. 415). However, for the best sample, No. 426, we obtain a value of K_1 of 0.69×10^4 erg/g, and for the sample No. 409, which contains some small amount of a higher oxide, a value of 1.75×10^4 erg/g. In all these cases the value of K_1 is much smaller than that of K_2 ($= 0.33 \times 10^7$ erg/g, as calculated by Kaplan⁽⁵⁾).

The above different values of K_1 for different samples cast a doubt on the validity of the present interpretation. To this adds another difficulty which we meet when we compare our values of K_1 with that derived by Keffer and O'Sullivan by analysing the field-depend-

ence of the powder susceptibility measured by Bizette, Squire and Tsai⁽³⁾. They obtained a value $K_1 = 5.8 \times 10^4$ erg/g at absolute zero (nine times their K_2 is our K_1 , and the value quoted here is twice as large as the corresponding value obtained earlier by Nagamiya⁽¹⁴⁾ by analysing the same data*) This value of K_1 deduced by Keffer and O'Sullivan, is about ten times the value obtained from the present torque measurements, and one might suspect that this difference could be due to the difference of the temperatures of the two experiments (0°K and 90°K). However, by analysing Bizette-Squire-Tsai's data at finite temperatures we find values of K_1 that are almost independent of temperature, falling down only very near the Néel temperature. If K_1 were a rapidly decreasing function of temperature, decreasing more rapidly than $(\chi_{\perp} - \chi_{\parallel})^2$ near the Néel temperature, as one might expect theoretically,** one would have obtained an increasing field dependence of the susceptibility with increasing temperature, whereas it decreased actually. In our experiment we observed also a decrease in torque amplitude when the temperature was raised above 90° to 113°K (Néel temperature), as shown in Fig. 7. All these facts indicate that the origin of K_1 may not be intrinsic. We shall therefore proceed to another possible interpretation in the next section.

§ 5. Interpretation of the Results, II.

Our samples may consist of small domains with different axes of magnetization. There may be walls of a certain structure (maybe similar to that of the ferromagnetic Bloch wall) which separate different domains. With the application of a magnetic field, these walls will move from their equilibrium positions and will give rise to a field-dependence of

the susceptibility, as pointed out by Néel⁽¹⁵⁾. Likewise, this movement will give rise to a variation in torque. We shall investigate the latter effect in this section.

Néel supposed a domain wall between two antiferromagnetic domains with different directions of the spin axis for the crystal which has more than one easy axes. If a magnetic field is applied, one of the domains whose spin axis is more perpendicular to the field will expand by pushing the wall to the side of the other domain, since the free energy decrease per unit volume of the former due to the applied field is greater than that of the latter, as $\chi_{\perp} > \chi_{\parallel}$. On the other hand, the wall will be exerted by an elastic restoring force, so that it will settle at a new equilibrium position. As in the case of an intrinsic anisotropy energy, this mechanism gives rise also to a field-dependence part of the susceptibility proportional to $(\chi_{\perp} - \chi_{\parallel})^2 H^2$.

Néel's idea can be applied to the present case in the following way. Let the direction cosines of the spin axis in one domain be α, β, γ and those in the other domain α', β', γ' . If the domain boundary wall shifts by a distance x , enlarging the first domain and diminishing the second one, the change of the energy of interaction with the external magnetic field will be

$$\frac{1}{2}(\chi_{\perp} - \chi_{\parallel})H^2[(\alpha\alpha' + \beta\beta' + \gamma\gamma')^2 - (\alpha'a + \beta'b + \gamma'c)^2]x \quad (7)$$

per unit area of the wall. We have to add to this the energy increase due to the restoring force, which may be written as

$$\frac{1}{2}cx^2. \quad (8)$$

Adding (8) to (7) and minimizing the total energy, we have

$$x = -\frac{1}{2c}(\chi_{\perp} - \chi_{\parallel})H^2[(\alpha\alpha' + \beta\beta' + \gamma\gamma')^2 - (\alpha'a + \beta'b + \gamma'c)^2]. \quad (9)$$

Substituting this x into the total energy increase per unit area, we have

$$-\frac{1}{8c}(\chi_{\perp} - \chi_{\parallel})H^4[(\alpha\alpha' + \beta\beta' + \gamma\gamma')^2 - (\alpha'a + \beta'b + \gamma'c)^2]. \quad (10)$$

It is seen that this expression is quartic in a, b, c . We now take the average of this expression by applying all the cubic symmetry

* Nagamiya used the formula which is valid for $K_1 = K_2$, whereas $K_1 \ll K_2$ in the present case, so that his previous value of K_1 has to be multiplied by 1/2. Thus Kaffer and O'Sullivan's value becomes four times as large. However, since their analysis is based on the formula which is valid for higher field strengths, their value may be more reliable.

** The anisotropy energy of six-fold symmetry within the easy plane of magnetization may mostly arise from the higher order dipole-dipole interaction, and so will vary as $(T_N - T)^n$, $n > 2$. The calculation of this quantity will be published in another paper.

operations. Physically this corresponds to having a cubic randomness for the domain distribution. However, since we do not know what the correlation between α, β, γ and α', β', γ' is for the neighboring domains, although there may be a finite number of direction for the spin axis within the crystal, we cannot arrive at a definite formula after the averaging. Nevertheless, we must have a formula of the following form:

$$-\text{const.}(\chi_{\perp} - \chi_{\parallel})^2 H^4 ((a^2 b^2 + b^2 c^2 + c^2 a^2) + \text{const.}) \quad (11)$$

It is seen, by comparing this expression with (5), that the present mechanism gives rise to the same field-dependence of the torque curve as that due to the intrinsic anisotropy energy. The first const. in (11) is proportional to the total area, A , of the wall participating in the present mechanism and inversely proportional to c . Thus, in order to explain our experimental results, c/A , has to be of order 10^4 erg/cm^3 (the previously derived value of K_1 being $\sim 10^4 \text{ erg/g}$, or $\sim 5 \times 10^4 \text{ erg/cm}^3$). Unfortunately, it is not possible at the present moment to estimate the value of c . Therefore, assuming rather arbitrarily that the linear dimension of the domains to be 10^{-3} cm , since Uchida and Kondoh observed on the surface of NiO (not in MnO) etch patterns of about 10 microns, we have $A \sim 10^3 \text{ cm}^2$ per cm^3 and correspondingly $c \sim 10^7 \text{ erg/cm}^4$.

It is not possible to conclude definitely at the present stage that the wall movement is responsible for the torque variation, though it is highly more probable than the mechanism due to the intrinsic anisotropy energy for the reasons given at the end of the preceding section.

Another conceivable mechanism is that the spin axis of each domain is constrained by those of the surrounding domains due to exchange interaction; this would give an effective anisotropy constant which corresponds to the previous K_1 . What actually governs the field dependence of the torque or susceptibility is the smallest one of the

three: the elasticity constant for the domain wall displacement, c/A , the elasticity constant for the rotation of the spin axis, arising from the interaction between domains, and the constant, K_1 , of the intrinsic anisotropy energy within the easy plane of magnetization.

The authors would like to express their sincere thanks to warm encouragement given by Professor Y. Mashiyama of University of Osaka Prefecture. They are also indebted to Mr. T. Hiwatari who helped us in X-ray photographing and Mr. N. Fukuoka who assisted us in magnetic measurements. A part of the present investigation was supported by a Scientific Research Expenditure of the Education Ministry.

References

- 1) T. Bizette, C. Squire, and B. Tsai: *Compt. rend* **207** (1938) 449.
- 2) T. Nagamiya, K. Yosida and R. Kubo: *Advance in Physics*, **4** no. 13, (1955).
- 3) C. G. Shull, W. A. Strauser and E. Q. Wollan: *Phys. Rev.* **83** (1951) 333.
- 4) W. L. Roth: *Phys. Rev.* **110** (1958) 1333; **111** (1958) 772.
- 5) J. I. Kaplan: *J. Chem. Phys.* **22** (1954) 1709.
- 6) F. Keffer and W. O'Sullivan: *Phys. Rev.* **180** (1957) 637.
- 7) N. C. Toms and H. P. Rooksby, *Nature* **165** (1950) 442.
- 8) T. Nagamiya: *State of Atoms in Magnetic Crystals*, read at the Second Welch Foundation Conference (Texas, Houston, Dec. 1958).
- 9) K. Kondoh, E. Uchida, Y. Nakazumi and T. Nagamiya: *J. Phys. Soc. Japan* **13** (1958) 579.
- 10) Y. Nakazumi: *Flame Fusion Synthesis of Large Single Crystals of MnO*, read at a symposium of Chem. Soc. Japan (Nagoya Tech. College, Nov. 6, 1958.)
- 11) R. W. G.: *Crystal Structure* **1** (1948).
- 12) *Standard X-ray Diffraction Powder Patterns*, N. B. S., 539, **5**.
- 13) S. Chikazumi: A paper read at a meeting of Phys. Soc. Japan (Tokyo, Apr. 2, 1959).
- 14) T. Nagamiya: *Progr. Theor. Phys.* **6** (1951) 342.
- 15) L. Néel: *Proceedings of the Kyoto Conference on Theoretical Physics, 1953* (Science Council of Japan, Tokyo, 1954).

Effect of Solvent on the Extension of High Polymer Molecule

By Hiroshi MIZUTANI

Department of Physics, Faculty of Science, Hokkaido University, Sapporo, Japan

(Received November 12, 1959)

For clarifying the physical properties of high polymer solution, it is important to investigate into the relation of the extension of high polymer molecule in solution to the potential energies between chain elements of the high polymer molecule and solvent molecules. In the present paper is given a theoretical treatment of this relation as a guide to the experimental study.

The calculation is based on a lattice model. The potential energies of interaction between chain elements and solvent molecules were formulated as precisely as possible, and the expression for the extension of high polymer molecule was obtained.

The results secured may be summarized as follows: The expression by which the end-to-end distance of high polymer molecule is related to the potential energies between chain elements and solvent molecules, and also the expression for a change in end-to-end distance of high polymer molecule, when it is put from vacuum into solution, have been obtained. From these relations we see that the quantity which determines the extension of high polymer molecule in solution is $\Delta E = (E_{pp} + E_{ss})/2 - E_{ps}$ and the quantity which determines the change in extension accompanying the transfer of high polymer molecule from vacuum to solution is $E_{ps} - E_{ss}/2$. Here $-E_{pp}$, $-E_{ss}$ and $-E_{ps}$ are the potential energy between two chain elements, that between two solvent molecules and that between a chain element and a solvent molecule, respectively.

§ 1. Introduction

In view of the fact that the extension of a high polymer molecule in solution varies according to the sort of solvent, it is anticipated that there must be some properties of a high polymer solution which depend on the extension of the high polymer molecule. Solvent-dependencies of viscosity, diffusion constant, viscoelastic properties and so on are the typical examples of such properties. Since it is to be considered that the effect of solvent on a dissolved high polymer molecule depends on the potential energy of interaction between chain element and solvent molecule, the inquiry into the relation between the molecular extension and the potential energy is not only of importance to the study of the real character of the extension but also necessary for investigating the chemico-physical nature of the high polymer solution.

The present paper deals with the theoretical investigation of this relation based on a lattice model. The results obtained, it is hoped, may serve as a guide to the experimental study to be promoted later.

The important points, which form the

keynote to the construction of the theory, are as follows:

- 1) The potential energy between the chain element of high polymer and the solvent molecule is calculated as rigorously as possible and introduced into the expression for the molecular extension r .

- 2) That the chain element has a finite volume is taken into account.

Now, the main experimental facts concerning the extension of a high polymer molecule in solution are

- 1) That the better the solvent, the greater the extension (end-to-end distance) of a high polymer molecule in this solvent:

- 2) That in a good solvent, the extension r becomes larger than 3.5 times $\sqrt{Nb^2}$ ¹⁾, where N being the number of chain elements, and b the mean bound length between two neighboring bound elements:

- 3) That in a good solvent, $dr/dT < 0$ ²⁾ (1)

- 4) That in a poor solvent, $dr/dT > 0$ ²⁾ (2)

- 5) That some solvents have positive heat of dissolution. (Heat of dissolution is the heat which is absorbed when a solute is dissolved in a solvent at a constant temperature.)

It is therefore to be desired to develop a theory for the extension of high polymer molecule, on which these experimental facts can be satisfactorily explained.

As a first step, let us inquire what kinds of force are necessary to be assumed in order to explain the experimental facts (1)~(5). Conceivable forces that act on or within a chain are as given in the following. All or some of these forces must be taken into consideration in formulating the theory, in so far as they are not contradictory to the existing facts.

F-1) Such a force within a chain with a fixed end-to-end distance, that causes the chain elements to take random distribution (elastic force giving rise to contraction of the chain).

F-2) Such a force within a chain that causes the line connecting the two ends of the chain to take random orientation (extensional force).

F-3) Repulsive force acting between neighboring chain elements due to volume exclusion of chain elements (extensional force).

F-4) Attractive molecular force between chain elements (contractive force).

F-5) Repulsive force between a chain element and a solvent molecule.

F-6) Attractive force between a chain element and a solvent molecule.

Extension of a high polymer chain in solution is determined by the balancing of these forces. When only the forces F-1) and F-2) are taken into account, the end-to-end distance r of a chain is given by

$$r = \sqrt{Nb^2} \quad (3)$$

where N is the number of chain elements, and b the effective bond length between neighboring elements. If account is taken of (F-3) and (F-4), besides (F-1) and (F-2), one gets

$$\left. \begin{array}{l} r \geq \sqrt{Nb^2}, \\ \text{according as} \end{array} \right\} \quad (4)$$

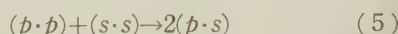
$$(F-3) \geq (F-4).$$

Thus it is clear that the smaller the force (F-4), the larger the extension of a chain, and vice versa.

Further, if the effects of (F-5) and (F-6) be to increase (decrease) the effect of (F-4), they will bring forth an additional contraction (extension) of the chain. In the case where the effect of solvent is disregarded, the extension of a chain involves only the

detachment of those elements which are not connected with each other directly with bond. But when the effect of the solvent is taken into consideration, the process that accompanies the extension of a chain must be the separation from each other not only of the elements but also of the solvent molecules, and the new creation of contacts between elements and solvent molecules.

Denote a chain element and a solvent molecule by p and s , respectively, then the above processes may be written as



If we express the potential energies between p and p , s and s , and p and s by $-E_{pp}$, $-E_{ss}$, and $-E_{ps}$, respectively, the energy necessary for these processes to occur is $E_{pp} + E_{ss} - 2E_{ps}$. Accordingly, the relations

$$E_{pp} \cong E_{pp} + E_{ss} - 2E_{ps} \text{ or } 2E_{ps} \cong E_{ss} \quad (6)$$

correspond to the case where the effect of solvent $\left\{ \begin{array}{l} \text{decreases} \\ \text{does not change} \\ \text{increases} \end{array} \right\}$ the effect of (F-4),

so that it $\left\{ \begin{array}{l} \text{increases} \\ \text{does not change} \\ \text{decreases} \end{array} \right\}$ the extension of

a high polymer chain in solution as compared with that in vacuum.

Thus, if these relations become known, we shall be able to gain a deeper insight into the behavior of the extension of high polymer chain in different solvents. Consider, for example, the case where all the intermolecular forces acting between chain elements and solvent molecules are dispersion forces. If we assume, for simplicity, that the volume of a chain element and that of a solvent molecule are nearly equal, we have

$$E_{ps} \cong \sqrt{E_{pp} \cdot E_{ss}} \quad (7)$$

so that relation (6) becomes

$$0 \cong \sqrt{E_{ss}} - 2\sqrt{E_{pp}} \text{ or } 4E_{pp} \cong E_{ss} \quad (8)$$

corresponding to $\left\{ \begin{array}{l} \text{increase} \\ \text{no change} \\ \text{decrease} \end{array} \right\}$ of the extension of chain in solution in comparison with that in vacuum. Thus, we see that, so far as the relation $4E_{pp} > E_{ss}$ holds for the dispersion force, the chain is more extended in solution than in vacuum, notwithstanding that the mixing heat of chain elements and solvent molecules is positive. Furthermore, from Eq. (4) it may well be anticipated that,

the effect of (F-3) is large enough, the extension of a chain in solution may become larger than 3.5 times $\sqrt{Nb^2}$.

Let us now inquire into the relation between the extension of chain and the temperature of solution. The chain element has a finite volume, which causes the increase of end-to-end distance r of the chain. Further, since the volume exclusion brings about diminution of configuration number, the tendency to contraction of the chain due to elastic force is repressed. Thus, the effect of volume exclusion leads to augmentation of r , which evidently becomes pronounced when the elements approach one another, as in the case of poor solvent.

Now, as the temperature rises, the increasing tendency to contraction of the chain due to elastic force and the expansion caused by the increase in volume of chain elements counteract each other. In case the former action predominates, the chain will shrink as is actually observed in good solvents, while when the latter action predominates, the chain will expand, which is the case with poor solvents.

We have thus seen that the assumption of the forces (F-1)~(F-6) fits in qualitatively with the experimental facts. It seems therefore amply justified to introduce such forces in formulating the theory of the extension of high polymer chain in solution.

§ 2. Theory of Extension of High Polymer Chain in Solution

The properties peculiar to high polymer solution are most conspicuously revealed by the solution with good solvent, where the high polymer chain has a large extension. The formulation of the theory must therefore be such that it can account for the behavior of high polymer chain in good solvents. There are many theories^{(3)~(18)} as to the extension of high polymer chain in vacuum, in which the forces (F-1), (F-2) and (F-3) are taken into consideration. There are, however, few theories^{(3),(19)} which takes account of (F-4) as well. Here we shall, for convenience's sake, take it for granted that the end-to-end distance r of the chain under the influence of forces (F-1), (F-2) and (F-3) is known and is equal to $\sqrt{CN\bar{v}}$, and then inquire into the question how this quantity will be modified

under the influence of forces (F-4), (F-5) and (F-6). The information as to the modification of $\sqrt{CN\bar{v}}$ makes it possible to see how r behaves in solution under the influence of forces (F-1)~(F-6) and to compare it with r in vacuum under the influence of forces (F-1)~(F-4).

The calculation of the extension of high polymer chain in solution will be performed in the following, being based on the lattice model and on the assumptions that the distribution of chain elements is Gaussian and that the solution is so diluted that the mutual interaction between high polymer molecules can be disregarded. Consider that the total solution is divided into equal volume cells whose number is equal to that of high polymer molecules in solution, that is, that each cell contains one high polymer molecule on the average. Statistical consideration of such cells will give the nature of the high polymer molecule in solution.

Mean square end-to-end distance of a chain is, on the assumption that energy E is a function of r , given by

$$\langle r^2 \rangle = \frac{\int r^2 \omega(E) \exp(-E/kT) dr}{\int \omega(E) \exp(-E/kT) dr}, \quad (9)$$

where $\omega(E)$ means the configuration number corresponding to E . Putting

$$\omega(E) = \omega(r) \quad (10)$$

and

$$S(r) = k \log \omega(r), \quad (11)$$

Eq. (9) can be rewritten as

$$\begin{aligned} \langle r^2 \rangle &= \frac{\int r^2 \exp \{ -(E(r) - TS(r))/kT \} dr}{\int \exp \{ -(E(r) - TS(r))/kT \} dr} \\ &= \frac{\int r^2 \exp(-F(r)/kT) dr}{\int \exp(-F(r)/kT) dr}. \end{aligned} \quad (12)$$

$S(r)$ and $E(r) - TS(r)$ correspond respectively to the entropy and the free energy of the system (cell) for given r . Thus, if we can calculate $E(r)$ and $S(r)$, and hence $F(r)$, we obtain $\langle r^2 \rangle$ from Eq. (12).

I) Calculation of entropy $S(r)$

Let the number of chain elements of a high polymer molecule and that of solvent

molecules in a cell be denoted by N and N_s , respectively. The entropy $S(r)$ of the cell is given by

$$S(r) = k \log \omega(r), \quad (13)$$

where $\omega(r)$ is the number of those configurations out of all possible configurations of the system which fulfil the condition that chain elements must be connected in series with each other, the end-to-end distance of the chain being fixed at r .

The probability that the end-to-end distance takes the value between r and $r+dr$ is given by

$$W_N(r)dr = \left(\frac{3}{2\pi CN^\gamma}\right)^{3/2} \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r^2 dr, \quad (14)$$

so that the configuration number of a chain with the end-to-end distance r is proportional to $W_N(r)$.

Further, since the volume of each cell V is far greater than that of a high polymer molecule V_r

$$V_r \ll V, \quad (15)$$

the number of position that the center of mass of a high polymer molecule can occupy in a cell may be put equal to the total number of lattice points of the cell, which is given by

$$\nu V = N + N_s, \quad (16)$$

ν being the density of lattice points. Thus the configuration number $\omega(r)$ of the system must be proportional to the product $W_N(r) \cdot \nu V$:

$$\begin{aligned} \omega(r) &= K \nu V W_N(r) \\ &= K(N + N_s) \left(\frac{3}{2\pi CN^\gamma}\right)^{3/2} \\ &\quad \times \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r^2, \end{aligned} \quad (17)$$

K being the proportionality constant, which means the total number of configuration of a chain for all possible values of r . Inasmuch as the configuration number of solvent molecules at the lattice points which are not occupied by the chain elements is unity, $\omega(r)$ given by (17) is none other than the configuration number of the whole system of a cell. Therefore we get the following expression for the entropy of the cell:

$$\begin{aligned} S(r) &= k \log \omega(r) \\ &= k \left\{ \log K(N + N_s) \left(\frac{3}{2\pi CN^\gamma}\right)^{3/2} \right. \end{aligned}$$

$$\left. -\frac{3r^2}{2CN^\gamma} + \log 4\pi r^2 \right\}. \quad (18)$$

II) Calculation of energy $E(r)$

First we calculate the number of pairs formed of chain elements (p) and solvent molecules (s) in volume V_r , exclusive of the pairs of two directly bonded chain elements. For the sake of simplicity, we assume that $p-s$ pairs exist only in V_r , which is permissible when the number of p is very large. In this case there exist $p-p$, $p-s$ and $s-s$ pairs inside the volume V_r and only $s-s$ pairs outside.

Putting the number of solvent molecules inside and outside of V_r equal to N_s^i and N_s^0 , respectively, we have

$$\left. \begin{aligned} N_s^i &= \nu V_r - N, \\ N_s^0 &= N_s - N_s^i = N_s - \nu V_r - N. \end{aligned} \right\} \quad (19)$$

Let σ be the number of the nearest neighbors around a lattice point, σ_p be the average number of p out of σ , and σ_s^i and σ_s^0 be the average numbers of s out of σ inside and outside of the volume V_r , respectively. Then

$$\left. \begin{aligned} \sigma_p &= \sigma \frac{N}{\nu V_r}, \\ \sigma_s^i &= \sigma \frac{\nu V_r - N}{\nu V_r}, \\ \sigma_s^0 &= \sigma. \end{aligned} \right\} \quad (20)$$

Now, the number of $p-p$ pairs (N_{pp}), excluding those chemically bonded along the chain, is on the average

$$N_{pp} = \frac{1}{2} N \sigma_p - N = \frac{\sigma N^2}{2\nu V_r} - N, \quad (21)$$

the number of $p-s$ pairs (N_{ps}), that of $s-s$ pairs inside and outside of V_r (N_{ss}^i , N_{ss}^0) and their sum ($N_{ss} = N_{ss}^i + N_{ss}^0$) come out to be

$$\left. \begin{aligned} N_{ps} &= N \sigma_s^i = N_s^i \sigma_p = \sigma N - \frac{\sigma N^2}{\nu V_r}, \\ N_{ss}^i &= \frac{1}{2} N_s^i \sigma_s^i = \frac{\sigma \nu V_r}{2} - \sigma N + \frac{\sigma N^2}{2\nu V_r}, \\ N_{ss}^0 &= \frac{1}{2} N_s^0 \sigma = \frac{\sigma}{2} (N_s - \nu V_r + N), \\ N_{ss} &= N_{ss}^i + N_{ss}^0 = \frac{\sigma}{2} (N_s - N) + \frac{\sigma N^2}{2\nu V_r}. \end{aligned} \right\} \quad (22)$$

It follows therefore that

$$\begin{aligned} E &= -N_{pp}E_{pp} - N_{ps}E_{ps} - N_{ss}E_{ss} \\ &= -\left(\frac{\sigma N^2}{2\nu V_r} - N\right)E_{pp} - \left(\sigma N - \frac{\sigma N^2}{\nu V_r}\right)E_{ps} \end{aligned}$$

$$\begin{aligned}
& -\left\{\frac{\sigma}{2}(N_s-N)-\frac{\sigma N^2}{2\nu V_r}\right\}E_{ss} \\
& =NE_{pp}-\sigma NE_{ps}-\frac{\sigma}{2}(N_s-N)E_{ss} \\
& \quad -\frac{\sigma N^2}{\nu V_r}\left(\frac{E_{pp}+E_{ss}}{2}-E_{ps}\right) \\
& =NE_{pp}-\sigma NE_{ps}-\frac{\sigma}{2}(N_s-N)E_{ss}-\frac{\sigma N^2}{\nu V_r}\Delta E,
\end{aligned} \tag{23}$$

where

$$\Delta E = \frac{E_{pp}+E_{ss}}{2} - E_{ps} \tag{24}$$

represents the heat absorbed by the system when chain elements are mixed with solvent molecules. Since, for the Gaussian distribution of chain elements, the mean square distance $\langle R^2 \rangle$ of chain elements from their center of mass is related to the mean square end-to-end distance $\langle r^2 \rangle$ of the chain by

$$\langle R^2 \rangle = \frac{1}{6} \langle r^2 \rangle. \tag{25}$$

we have

$$V_r = \frac{4\pi}{3} R^3 = \frac{4\pi}{3} (1/6)^{3/2} r^3 = \tau r^3. \tag{26}$$

Whence we get

$$E(r) = NE_{pp} - \sigma NE_{ps} - \frac{\sigma}{2}(N_s-N)E_{ss} - \frac{\sigma N^2}{\nu\tau}\Delta E r^{-3}. \tag{27}$$

III) Free energy $F(r)$

From Eqs. (18) and (27), we obtain the expression for the free energy of the whole system as a function of end-to-end distance r of high polymer molecule;

$$\begin{aligned}
F(r) &= E(r) - TS(r) \\
&= NE_{pp} - \sigma NE_{ps} - \frac{\sigma}{2}(N_s-N)E_{ss} \\
&\quad - \frac{\sigma N^2}{\nu\tau}\Delta E r^{-3} - kT \left\{ \log K(N+N_s) \right. \\
&\quad \times \left. \left(\frac{3}{2CN^\gamma} \right)^{3/2} - \frac{3r^3}{2CN^\gamma} - \log 4\pi r^2 \right\}.
\end{aligned} \tag{28}$$

IV) Mean square end-to-End distance of a chain $\langle r^2 \rangle$

By Eqs. (12) and (28), we obtain

$$\langle r^2 \rangle_s = \frac{\int \exp \left\{ \frac{\sigma N^2}{\nu\tau} \frac{\Delta E}{kT} r^{-3} \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^4 dr}{\int \exp \left\{ \frac{\sigma N^2}{\nu\tau} \frac{\Delta E}{kT} r^{-3} \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^2 dr}, \tag{29}$$

or, by making use of the expansion formula

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots, \tag{30}$$

$$\begin{aligned}
\langle r^2 \rangle_s &= CN^\gamma \frac{1 + \frac{1}{CN^\gamma} \left[\int \left\{ \frac{\sigma N^2}{\nu\tau} \frac{\Delta E}{kT} r^{-3} + \frac{1}{2!} \left(\frac{\sigma N^2}{\nu\tau} \right)^2 \left(\frac{\Delta E}{kT} \right)^2 r^{-6} + \dots \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^4 dr \right]}{1 + \left[\int \left\{ \frac{\sigma N^2}{\nu\tau} \frac{\Delta E}{kT} r^{-3} + \frac{1}{2!} \left(\frac{\sigma N^2}{\nu\tau} \right)^2 \left(\frac{\Delta E}{kT} \right)^2 r^{-6} + \dots \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^2 dr \right]}.
\end{aligned} \tag{31}$$

In case the second and higher terms are small compared with the first term both in the numerator and denominator, Eq. (31) can be rewritten as

$$\begin{aligned}
\langle r^2 \rangle_s &= CN^\gamma \left[1 + \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \frac{\sigma N^2}{\nu\tau} \frac{\Delta E}{kT} \left\{ \frac{1}{CN^\gamma} \int \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r dr \right. \right. \\
&\quad \left. \left. - \int \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^{-1} dr \right\} + \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \frac{1}{2!} \left(\frac{\sigma N^2}{\nu\tau} \right)^2 \left(\frac{\Delta E}{kT} \right)^2 \right. \\
&\quad \left. \times \left\{ \frac{1}{CN^\gamma} \int \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^{-2} dr - \int \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^{-4} dr \right\} + \dots \right].
\end{aligned} \tag{32}$$

From this we can estimate the deviation of $\langle r^2 \rangle_s$ from CN^γ as affected by the potential energy between chain elements and solvent molecules.

Take, as an example, polystyrene with molecular weight 200,000 (molecular weight

of the chain element=54). As the second and higher terms in the square brackets of Eq. (32) are the correction terms, we may well substitute Nb^2 for CN^γ in these terms, b being the effective bound length, which takes the value $b=8.5 \times 10^{-8}$ cm for polystyrene. Eq. (32) then becomes

$$\langle r^2 \rangle_s = CN^\gamma \left[1 - 82.2 \frac{\sigma \Delta E}{kT} - 2.35 \times 10^4 \left(\frac{\sigma \Delta E}{kT} \right)^2 \dots \right]. \quad (33)$$

In so far as $\sigma \Delta E/kT \cong 10^{-3}$, consideration up to the second terms is sufficient. Thus we see that in the case of the solvent which dissolves polystyrene with absorption of heat, namely $\Delta E > 0$,

$$\langle r^2 \rangle_s < CN^\gamma. \quad (34)$$

As for the temperature dependency of r we can say as follows;

(I) In case $\Delta E > 0$, we get, rewriting Eq. (33) in the form

$$\langle r^2 \rangle_s = CN^\gamma A(E), \quad (35)$$

$$\frac{dA(E)}{dT} > 0. \quad (36)$$

It holds, on the other hand, that

$$\frac{dCN^\gamma}{dT} < 0. \quad (37)$$

Consequently, the temperature dependency of extension of high polymer molecule dr/dT is determined by the balance between the relations (36) and (37), namely

$$\left. \begin{aligned} \left| \frac{dCN^\gamma}{dT} \right| &> \frac{dA(E)}{dT} \text{ for good solvent,} \\ \text{and} \\ \left| \frac{dCN^\gamma}{dT} \right| &< \frac{dA(E)}{dT} \text{ for poor solvent.} \end{aligned} \right\} \quad (38)$$

(II) If $\Delta E < 0$,

$$\frac{dA(E)}{dT} < 0, \quad (39)$$

so that, in combination with the relation (37) which holds likewise in this case, we always have $dr/dT < 0$, as is the case with good solvent.

§ 3 Theory of Extension of High Polymer Chain in Vacuum

In vacuum the forces (F-1)~(F-4) come into question. We must estimate the effect which the force (F-4) brings about on the square end-to-end distance CN^γ of high polymer chain under the forces (F-1)~(F-3). Also in this case, the mean square end-to-end distance $\langle r^2 \rangle$ and the entropy $S(r)$ of the chain, which is equal to that in solution, can be written in the forms of Eq. (12) and (18), respectively. The energy of the system E is composed of potential energies of p - p pairs, so that, since the number of p - p pairs is given by Eq. (21), we get

$$\begin{aligned} E &= -N_{pp}E_{pp} = -\frac{\sigma N^2}{2\nu V_r}E_{pp} - NE_{pp} \\ &= -\frac{\sigma N^2 E_{pp}}{2\nu \tau} r^{-3} - NE_{pp}. \end{aligned} \quad (40)$$

Thus the free energy of the system comes out, by Eqs. (40) and (18) to be

$$\begin{aligned} F(r) &= -\frac{\sigma N^2 E_{pp}}{2\nu \tau} r^{-3} - NE_{pp} \\ &\quad - kT \left[\log K(N+N_s) \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \right. \\ &\quad \left. - \frac{3r^2}{2CN^\gamma} + \log 4\pi r^2 \right], \end{aligned} \quad (41)$$

and hence, by (12)

$$\langle r^2 \rangle_v = \frac{\int \exp \left\{ \frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} r^{-3} - N \frac{E_{pp}}{kT} \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^4 dr}{\int \exp \left\{ \frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} r^{-3} - N \frac{E_{pp}}{kT} \right\} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^2 dr} \quad (42)$$

or, by making use of the expansion

$$\begin{aligned} e^x &= 1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots, \\ \langle r^2 \rangle_v &= CN^\gamma \frac{1 + \frac{1}{CN^\gamma} \left[\frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} r^{-3} + \frac{1}{2!} \left(\frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} \right)^2 r^{-6} + \dots \right] \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^4 dr}{1 + \left[\frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} r^{-3} + \frac{1}{2!} \left(\frac{\sigma N^2}{2\nu \tau} \frac{E_{pp}}{kT} \right)^2 r^{-6} + \dots \right] \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \exp \left(-\frac{3r^2}{2CN^\gamma} \right) 4\pi r^2 dr}. \end{aligned} \quad (43)$$

If the second and higher terms are very small compared with the first term both in numerator and denominator of Eq. (43), this equation reduces to

$$\begin{aligned} \langle r^2 \rangle_v = & CN^\gamma \left[1 + \frac{\sigma N^2}{2\nu\tau} \frac{E_{pp}}{kT} \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \right. \\ & \times \left\{ \frac{1}{CN^\gamma} \int \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r dr \right. \\ & \left. - \int \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r^{-1} dr \right\} \\ & + \frac{1}{2!} \left(\frac{\sigma N^2}{2\nu\tau} \frac{E_{pp}}{kT} \right)^2 \left(\frac{3}{2\pi CN^\gamma} \right)^{3/2} \\ & \times \left\{ \frac{1}{CN^\gamma} \int \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r^{-2} dr \right. \\ & \left. \int \exp\left(-\frac{3r^2}{2CN^\gamma}\right) 4\pi r^{-4} dr \right\} + \dots \left. \right]. \quad (44) \end{aligned}$$

Putting Nb^2 in place of CN^γ in the second and higher terms, for the same reason as before, we apply Eq. (44) to the case of polystyrene of molecular weight 200,000, obtaining

$$\begin{aligned} \langle r^2 \rangle_v = & CN^\gamma \left[1 - 82.2 \frac{\sigma E_{pp}}{2kT} \right. \\ & \left. - 2.35 \times 10^4 \left(\frac{\sigma E_{pp}}{2kT} \right)^2 \dots \right]. \quad (45) \end{aligned}$$

From this we see that the end-to-end distance r in vacuum is smaller than $\sqrt{CN^\gamma}$.

§ 4 Comparison of $\langle r^2 \rangle_s$ with $\langle r^2 \rangle_v$

The relation between the end-to-end distance r of a high polymer molecule in vacuum and that in solution can be obtained by comparing Eq. (33) with Eq. (45). If it holds that

$$\frac{\sigma \Delta E}{kT}, \quad \frac{\sigma E_{pp}}{2kT} \cong 10^{-3} \quad (46)$$

the ratio of $\langle r^2 \rangle_s$ to $\langle r^2 \rangle_v$ takes a very simple form;

$$\begin{aligned} \frac{\langle r^2 \rangle_s}{\langle r^2 \rangle_v} & \cong \frac{1 - 82.2 \frac{\sigma \Delta E}{kT} - 2.35 \times 10^4 \left(\frac{\sigma \Delta E}{kT} \right)^2}{1 - 82.2 \frac{\sigma E_{pp}}{2kT} - 2.35 \times 10^4 \left(\frac{\sigma E_{pp}}{2kT} \right)^2} \\ & \cong 1 + 82.2 \frac{\sigma}{kT} \left(E_{ps} - \frac{E_{ss}}{2} \right) \\ & + 2.35 \times 10^4 \left(\frac{\sigma}{kT} \right)^2 \left(E_{ps} - \frac{E_{ss}}{2} \right) \\ & \times \left(E_{pp} + \frac{E_{ss}}{2} - E_{ps} \right). \end{aligned}$$

Whence we obtain:

$$\left. \begin{aligned} \langle r^2 \rangle_s & \cong \langle r^2 \rangle_v, \\ \text{according as} \\ E_{ps} - \frac{E_{ss}}{2} & \cong 0. \end{aligned} \right\} \quad (48)$$

If the intermolecular force is dispersion force, the relation (48) becomes, by virtue of Eq. (7)

$$\left. \begin{aligned} \langle r^2 \rangle_s & \cong \langle r^2 \rangle_v \\ \text{according as} \\ 4E_{pp} - E_{ss} & \cong 0. \end{aligned} \right\} \quad (49)$$

The relations (48) and (49) are valid only for the case where the condition (46) is satisfied.

When

$$\frac{\sigma \Delta E}{kT}, \quad \frac{\sigma E_{pp}}{2kT} > 10^{-3}, \quad (50)$$

it becomes necessary to compare Eq. (29) directly with Eq. (42). These equations have close resemblance to each other and can be written in the form

$$Z(A) = \frac{\int e^{Ar^{-3}} e^{-Br^2} r^4 dr}{\int e^{Ar^{-3}} e^{-Br^2} r^2 dr}. \quad (51)$$

As can easily be proved (see Appendix) function $Z(A)$ is a monotonously decreasing function of A , so that

$$\left. \begin{aligned} Z(A_1) & \cong Z(A_2), \\ \text{according as} \\ A_1 & \cong A_2. \end{aligned} \right\} \quad (52)$$

Thus, from Eqs. (29) and (42), we get

$$\left. \begin{aligned} \langle r^2 \rangle_s & \cong \langle r^2 \rangle_v, \\ \text{according as} \\ \Delta E & \cong \frac{E_{pp}}{2} \end{aligned} \right\} \quad (53)$$

or,

$$\left. \begin{aligned} \langle r^2 \rangle_s & \cong \langle r^2 \rangle_v \\ \text{according as} \\ E_{ps} - \frac{E_{ss}}{2} & \cong 0, \end{aligned} \right\} \quad (53')$$

which is identical with the relation (48).

§ 5 Discussion

The above theory, in which the increase of chain extension r due to the finite volume of chain element is expressed in the form $\sqrt{CN^\gamma}$, merely gives the deviation of r in solution from $\sqrt{CN^\gamma}$. In order to obtain the absolute value of r , it is necessary to know the correct value of CN^γ , which is not accessible at the present stage of the theory.

The theory is based on the assumption that the distribution of chain elements is Gaussian such that the mean square end-to-end distance is CN^{γ} , but the actual distribution must be different from Gaussian, since in the Gaussian distribution the superposition of elements is not excluded notwithstanding that the augmentation of chain extension arising from the effect of volume exclusion is taken into account. This difference in distribution manifests its effect only little in the case where the chain extension is large, while it will become of importance when the extension diminishes so that the chain elements come in contact with each other at many places. In other words, the theory will prove more and more inaccurate as it is applied to poorer solvent.

As for the temperature dependency of r it is determined by the following properties:

(1) Tendency toward contraction of chain due to elastic effect is strengthened with rising temperature.

(2) Volume exclusion effect causes the configuration number of the chain to decrease, so that, the elastic force of the chain is diminished.

(3) The higher the temperature, the more the increment of excluded volume of chain elements.

For rigorous treatment of the effects (2) and (3), Gaussian approximation for the distribution of chain elements is not sufficient. Gaussian distribution may be assumed solely in such a case that the effects (2) and (3) are insignificant and it suffices to take only the effect (1) into consideration, namely, in the case of good solvent.

In short, the present theory which is based

on the assumption of Gaussian distribution of chain elements proves to be an approximate theory applicable only to the case of good solvent.

Further it is to be noticed that since the Bragg-Williams approximation forms the basis of the theory, the forward step to be taken must be to use Bethe approximation for refining the theory.

Nevertheless, we have obtained several fruitful results, as stated in the foregoing. It will therefore not be insignificant to examine the availability of the theory through comparison with experimental facts.

We have seen that the quantity which determines the relations between $\langle r^2 \rangle_s$ and CN^{γ} is ΔE , and those which determine the relations between $\langle r^2 \rangle_s$ and $\langle r^2 \rangle_v$ are E_{ps} and E_{ss} (or E_{pp} and E_{ss} when the force acting between the elements is dispersion force). Thus in order to scrutinize the theory, it is necessary to obtain available data concerning $\langle r^2 \rangle_s$, ΔE , E_{ss} , E_{pp} and the like. As we have at present very few systematic data as regards these quantities, we are now carrying on experimental determination of them. The results will be reported in the near future.

Appendix

Eqs. (29) and (42) can be expressed in the common form (51)

$$Z(A) = \frac{\int e^{Ar^{-3}} e^{-Br^2} r^4 dr}{\int e^{Ar^{-3}} e^{-Br^2} r^2 dr},$$

where A is a factor involving intermolecular potential energy. By examining the sign of $dZ(A)/dA$.

$$\frac{dZ(A)}{dA} = \frac{\left\{ \int e^{Ar^{-3}} e^{-Br^2} r^2 dr \right\} \left\{ e^{Ar^{-3}} e^{-Br^2} r^4 dr \right\} - \left\{ \int e^{Ar^{-3}} e^{-Br^2} r^4 dr \right\} \left\{ \int e^{Ar^{-3}} e^{-Br^2} r^{-1} dr \right\}}{\left\{ \int e^{Ar^{-3}} e^{-Br^2} r^2 dr \right\}^2}, \quad (54)$$

we can determine whether $Z(A)$ is an increasing or a decreasing function of A .

Let the numerator of Eq. (54) be X , then

$$\begin{aligned} X &= \iint e^{A(x^{-3}+y^{-3})} e^{-B(x^2+y^2)} (x^2y - x^4y^{-1}) dx dy \\ &= \int_{y>y} \int e^{A(x^{-3}+y^{-3})} e^{-B(x^2+y^2)} (x^2y - x^4y^{-1} + y^2x - y^4x^{-1}) dx dy \\ &= - \int_{x>y} \int e^{A(x^{-3}+y^{-3})} e^{-B(x^2+y^2)} x^{-1}y^4(xy^{-1}-1)^2(xy^{-1}+1)(x^2y^{-2}+xy^{-1}+1) dx dy > 0. \end{aligned} \quad (55)$$

thus we have

$$\frac{dZ(A)}{dA} < 0. \quad (56)$$

Acknowledgment

The author wishes to express his hearty thanks to Prof. T. Hori for his kind discussion on the present subject.

References

- 1) P. Debye and A. M. Bueche: *J. Chem. Phys.* **16** (1948) 573.
- 2) B. H. Zimm: *J. Chem. Phys.* **16** (1948) 1099.
- 3) P. J. Flory: *J. Chem. Phys.* **17** (1949) 303.
- 4) K. Suzuki: *Bull. Chem. Soc. Japan* **22** (1949) 8.
- 5) E. W. Montroll: *J. Chem. Phys.* **18** (1950) 734.
- 6) H. L. Frisch, F. C. Collins and B. Friedman: *J. Chem. Phys.* **19** (1951) 1402.
- 7) E. Teramoto: *Busseiron Kenkiu* (in Japanese) **42** (1951) 24.
- 8) M. Yamamoto: *Busseiron Kenkiu* (in Japanese) **44** (1951) 36.
- 9) J. J. Hermans, M. S. Klamkin and R. Ullman: *J. Chem. Phys.* **20** (1952) 1360.
- 10) T. B. Grimley: *J. Chem. Phys.* **21** (1953) 185.
- 11) F. Bueche: *J. Chem. Phys.* **21** (1953) 205.
- 12) H. M. James: *J. Chem. Phys.* **21** (1953) 1628.
- 13) B. H. Zimm, W. H. Stockmayer and M. Fixman: *J. Chem. Phys.* **21** (1953) 1716.
- 14) F. T. Wall: *J. Chem. Phys.* **21** (1953) 1914.
- 15) M. N. Rosenbluth and A. W. Rosenbluth: *J. Chem. Phys.* **23** (1955) 356.
- 16) M. Fixman: *J. Chem. Phys.* **23** (1955) 1656.
- 17) W. R. Krigbaum: *J. Chem. Phys.* **23** (1955) 2113.
- 18) F. T. Wall: *J. Chem. Phys.* **30** (1959) 634.
- 19) P. J. Flory and T. G. Fox, Jr.: *J. Amer. Chem. Soc.* **73** (1951) 1904.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 3, MARCH, 1960

Paramagnetic Susceptibility of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and its Deuterated Salts

By Taiichiro HASEDA

*The Research Institute for Iron, Steel and Other Metals
Tohoku University, Sendai, Japan*

(Received November 13, 1959)

The paramagnetic susceptibility of a single crystal of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was measured by the usual a-c bridge method. Transition to the antiferromagnetic state was observed at about 3.3°K. The easy axis is along the crystalline c axis. The g values determined in the paramagnetic region, below 20°K are: $g_0 = g_b = 4.9$ and $g_{c\perp} = 2.9$. Some considerations about the anisotropic susceptibilities in the paramagnetic state are given from the standpoint of crystalline field theory. The exchange interaction in this salt is discussed considering the interaction path between the magnetic ions which involves the linkages of chlorine atoms or water molecules. The measurements on the deuterated salts are intended to make clear the effect of the hydrogen bond on the magnetic exchange interaction.

§ 1. Introduction

It was reported by Haseda and Kanda¹⁾ that the susceptibilities of powdered samples of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ show antiferromagnetic behaviour below about 3°K. Crystal analysis was undertaken by Mizuo, Ukei and Sugawara, and it was found that each Co^{+2} ion is surrounded by four water molecules in a plane and by

two chlorine atoms along the axis perpendicular to the plane²⁾. Measurements of paramagnetic resonance were attempted by Date³⁾ and also by Gerritzen⁴⁾. Recently, Date has succeeded in detecting the paramagnetic and antiferromagnetic resonance in this salt in the frequency range of 9.5 to 38 GC/sec³⁾. Sugawara has detected the proton resonance

According to the relation to the next nearest water molecules, and therefore two Co^{+2} ions in a unit cell are almost magnetically equivalent in this salt.

From the values of the anisotropic susceptibilities in the paramagnetic state, (below 20°K) the g -values of each axis are determined using the relation of the Curie-Weiss law with $T = 3.3^\circ\text{K}$. The values obtained are $g_{\parallel} = 4.9$, $g_{\perp} = 4.9$ and $g_{\text{av}} = 2.9$. Because of the limited range of temperatures within which the Curie-Weiss law holds (below 20°K down to 4°K), the g -values are not determined with sufficient accuracy. However, it is interesting to compare these values with those found in $\text{CoNH}_4\text{-Tutton}$ salt. In Table II, the g -values in these two salts are given. Contrary to the case of $\text{CoNH}_4\text{-Tutton}$ salt, the g -value of the axial direction ($g_{\parallel}$), which is along $\text{Cl-Co}^{+2}\text{-Cl}$ direction in this case, is smaller than the values in the plane perpendicular to the axis ($g_{\perp}$ and g_{av}).

Table II. g -values of $\text{CoNH}_4\text{-Tutton}$ salt and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

	g -values	
$\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}^*$	$g_z = 6.45 \pm 0.13$	$g_{\text{min}} = g_y = 3.06 \pm 0.06$
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	$g_{\perp} = 2.9$	$g_{\parallel} = g_{\text{av}} = 4.9$

* B. Bleaney and D. J. E. Ingram: Proc. Roy. Soc. **208** (1951) 143.

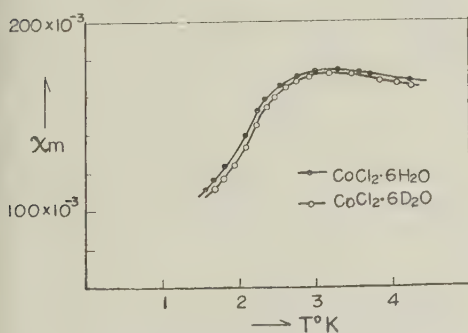


Fig. 3. Molar susceptibility of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{D}_2\text{O}$.

The field dependence of susceptibility and the paramagnetic relaxation effect are not detected in the paramagnetic or antiferromagnetic state up to the field of 1200 gauss and to 1500 c/s.

Besides the measurements on single crystals, the susceptibilities of powdered sample of

$\text{CoCl}_2 \cdot 6\text{D}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{D}_2\text{O}$ were observed. The results are shown in Fig. 3 and Fig. 4. Any appreciable change in the transition temperature from the case of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was not detected. The discussion is given in § 3-(3).

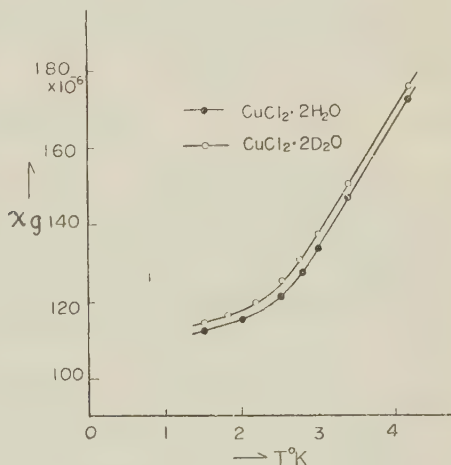
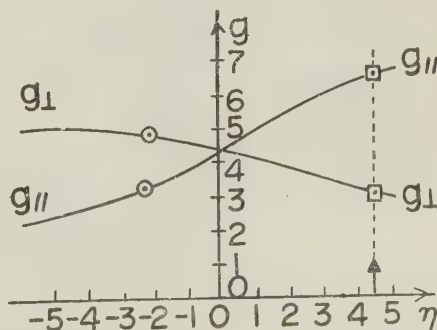


Fig. 4. Molar susceptibility of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{D}_2\text{O}$.

§ 3. Discussions

(1) Paramagnetic susceptibility of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Kambe, Koide and Usui calculated the energy levels of Co^{+2} ion in the crystalline field of tetragonal symmetry and gave the expression for the anisotropic g -values as a function of crystalline field parameters. Their results were compared with the experiment on the $\text{CoNH}_4\text{-Tutton}$ salt. Reasonable agreement was obtained, though some difficulties remained, as the authors themselves pointed



■ Experimental values of $\text{CoNH}_4\text{-Tutton}$ Salt
○ Experimental values of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Fig. 5. Variation of $g_{\parallel}$ and $g_{\perp}$ with η . (by Kambe, Koide and Usui. 1952).

out. The g -values obtained are shown in Fig. 5. $g_{//}$ and $g_{\perp}$ are the g -values in directions parallel and perpendicular to the tetragonal axis respectively. The abscissa η in Fig. 5 is given as

$$\eta = \frac{\delta}{\lambda} = \frac{1}{\lambda} \left\{ \frac{10}{35} e \langle Q r^4 \rangle + \frac{12}{35} e \langle A r^2 \rangle \right\}, \quad (1)$$

Q and A used here are the crystalline field parameters in the expression

$$V_{crys} = e \sum_i \left\{ A(x_i^2 + y_i^2 + z_i^2) + D(x_i^4 + y_i^4 + z_i^4) + Q(z_i^4 + 6x_i^2 y_i^2) + \dots \right\}, \quad (2)$$

λ is the spin-orbit coupling constant.

As is shown in Fig. 5, in the usual octahedrally coordinated compound such as $\text{CoNH}_4\text{-Tutton salt}$, $g_{//}=6.2$ and $g_{\perp}=3.0$, corresponding to the η -values of 3.5~4.5.

Contrary to these cases, in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $g_{//}=2.9$ and $g_{\perp}=4.9$, corresponding to the η -values of about -4.0

The calculation of the crystalline field parameters was attempted by Van Vleck⁷⁾ and Polder⁸⁾ in a rather crude model (point charge or point dipole model with octahedral coordination). A more elaborate calculation was made by Kleiner⁹⁾ and recently by Sugano and Tanabe¹⁰⁾. The simple method gives consistent values for the parameters of the crystalline field, but the more elaborate method gives rather inconsistent results. Although it is clear now that the simple method such as used by Polder is not a reliable one, it will be worth-while to check

the method in the case of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ where the anisotropy in g -values is very different qualitatively from the case of the $\text{CoNH}_4\text{-Tutton salt}$.

The model used is shown in Fig. 6. Here each chlorine ion is treated as a point charge, and each water molecule as a point dipole. Tetrahedral crystalline field parameters are represented by the following formulas.

$$\left. \begin{aligned} A &= -3 \left(\frac{\mu_a}{a^4} - \frac{\mu_b}{b^4} \right) + \left(\frac{e_a}{a^3} - \frac{e_b}{b^3} \right) \\ D &= -\frac{25}{4} \left(\frac{4\mu_a}{a^6} + \frac{3\mu_b}{b^6} \right) + \frac{5}{4} \left(\frac{4e_a}{a^5} + \frac{3e_b}{b^5} \right) \\ Q &= +\frac{25}{4} \left(\frac{\mu_a}{a^6} - \frac{\mu_b}{b^6} \right) - \frac{5}{4} \left(\frac{e_a}{a^5} - \frac{e_b}{b^5} \right) \end{aligned} \right\} \quad (3)$$

A , D and Q are the parameters which appeared in equation (2). μ_a , e_a , a , etc. are given in Fig. 6. In Table III, the calculated values are given for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoNH}_4\text{-Tutton salt}$. The values of η obtained by the use of equation (1) are also given in Table III. From the theory of Kambe, Koide and Usui, reasonable agreement with the experimental results is obtained as is seen in Fig. 5. Though this agreement may be fortuitous considering the approximation used, the result will have qualitative meaning.

(2) Antiferromagnetic state in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Interaction paths

As is mentioned in §2, the axis of easy magnetization is almost along the crystalline c axis. It is interesting to note that in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ which is isomorphous to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and is also antiferromagnetic below 6°K¹¹⁾, the easy axis is along the c_1 axis.

The superexchange interaction (which amounts to about 3°K.) between two adjacent Co^{+2} ions in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ which are in the same (001) plane is thought to follow the following linkage (or path) of atoms:

Table. III. Calculated values of η in Eq. (1).

	$\text{CoNH}_4\text{-Tutton salt}$	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
A	-0.28×10^{14}	$-0.06 \times 10^{14} (+0.10 \times 10^{14})^*$
Q	-0.22×10^{30}	$-0.01 \times 10^{30} (+0.02 \times 10^{30})^*$
η^{**}	-4.5	-1.0 (-5.0)

* Values in brackets are obtained using the constants in brackets in Fig. 6.

** Values of $\langle r^4 \rangle$ and $\langle r^2 \rangle$ used in the calculation are 0.70×10^{-32} and 0.80×10^{-16} respectively.

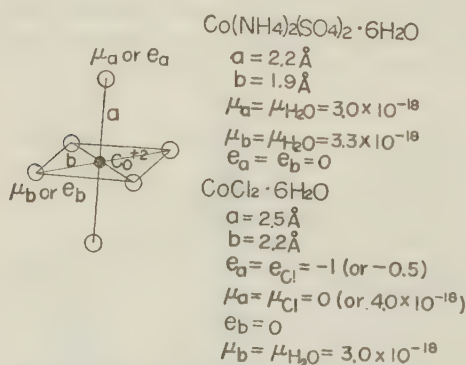
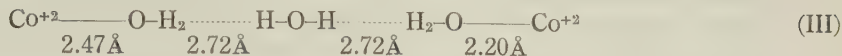
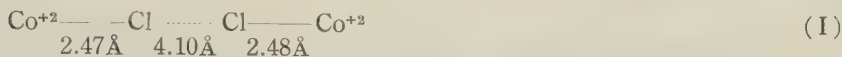
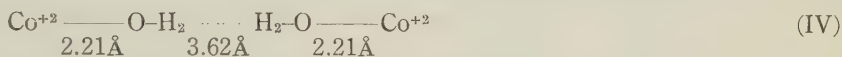


Fig. 6. Constants used for calculation of the crystalline field. Values of each μ involve the induced polarization due to the Co^{+2} ion. Two sets of values of e_a and μ_a in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are used. The best fit will be obtained midway between these two cases.

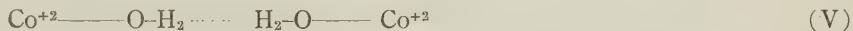


The path of superexchange interaction between two Co^{+2} ions, each on two adjacent (001) layers, is thought to be



Distinct cleavage on a (001) plane shows weak bonding between the layers of (001) planes²⁾. It may be said that the superexchange interaction is also weak between (001) layers. We can estimate the order of the interaction energy on the path (IV) comparing it with the path in Tutton salt.

In Tutton salt, each Co^{+2} ion is surrounded by six water molecules octahedrally, so the nearest interaction path is necessarily



The superexchange interaction through this linkage may be considered comparable with that through the path IV in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The fact that the magnetic transition occurs usually at about 0.1°K in the Tutton salts such as $\text{CoNH}_4(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{MnNH}_4(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, means that the order of magnitude of the interaction on path IV or path V will be about 0.1°K. If this order is accepted for the path IV in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, we can conclude that the main part of the interaction comes from the paths I, II and perhaps from III. Here, it will be worth-while to note the existence of a hydrogen bond in path III*.

(3) Effect of the hydrogen bond on magnetic interaction

Geller and Bond¹²⁾ have pointed out the importance of the hydrogen bond in the superexchange interaction in the case of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$. In our case, as was mentioned in the forgoing section, the superexchange interaction between two magnetic ions will be in the paths such as I, II, etc. The overlap of the electron cloud of atoms or molecules which are situated between two magnetic ions is thought to be dominant in these paths.

Though the details of the electronic structure of the hydrogen bond has not been clarified, it will be supposed that the hydrogen

bond may give also some special effect in the superexchange interaction in the case of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The measurements on the deuterated salts, such as $\text{CoCl}_2 \cdot 6\text{D}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{D}_2\text{O}$ were made to detect this effect. The results were negative, not showing any appreciable change of the transition point in these salts. These facts mean either that the effect of the hydrogen bond is not dominant in the salts investigated, or that the effect of the hydrogen bond on the superexchange interaction is not altered when hydrogen is replaced by deuterium in this bond.

The author wishes to express his sincere thanks to Prof. Kanda for his continuous interest and encouragement on this problem. He also wishes to thank to Mr. Takashi Sato for helpful assistance in the experiments.

Note added in proof. Private communication from Dr. S. A. Friedberg tells us that he and his collaborator have made the measurement of susceptibility of a single crystal of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Their results are in reasonable agreement with ours.

References

- 1) T. Heseda and E. Kanda: J. Phys. Soc. Japan **12** (1957) 1051.
- 2) J. Mizuno, K. Ukei and T. Sugawara: J. Phys. Soc. Japan **14** (1959) 383.
- 3) M. Date: J. Phys. Soc. Japan **14** (1959) 1244.

* The formation of a hydrogen bond in path II is doubtful from the distance and bond angles.

- 4) H. J. Gerritzen: Thesis, Leiden 1955.
- 5) T. Sugawara: J. Phys. Soc. Japan **14** (1959) 1248.
- 6) K. Kambe, S. Koide and T. Usui: Progr. Theor. Phys. **7** (1952) 15.
- 7) J. H. Van Vleck: J. Chem. Phys. **7** (1939) 61.
- 8) D. Polder: Physica **9** (1942) 709.
- 9) W. H. Kleiner: J. Chem. Phys. **20** (1952) 1784.
- 10) S. Sugano and Y. Tanabe: J. Phys. Soc. Japan **11** (1956) 864.
- 11) T. Haseda, H. Kobayashi and M. Date: J. Phys. Soc. Japan **14** (1959) 1724.
- 12) S. Geller and W. L. Bond: J. Chem. Phys. **29** (1958) 925.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 3, MARCH, 1960

Photo- and Thermochemical Reactions in Potassium Chloride Crystals—— A Quantitative Study of the M Centre ——

By Tetsuhiko TOMIKI

*The Department of Physics, The Faculty of Science, Tohoku University,
Sendai, Japan*

(Received September 16, 1959)

By experiments upon the thermal stability of the M, R and N centres in KCl crystal coloured additively, it was revealed that R_1 and R_2 centres dissociated thermally into F, M and N centres above 50°C , N centres dissociate into F and M centres above 100°C and M centres dissociated into F centres above 130°C . The relaxation time τ for the dissociation process of the M centre is expressed by $1/\tau = 2 \cdot 10^{12} \times \exp(-1.31/kT) \text{ sec}^{-1}$ for kT in ev. The corresponding experiment on the R centre was unsuccessful. With use of the above properties of photochemical products, the number of the F centre corresponded to one M centre was determined with high precision. In addition to this, the quantum yield of the M centre in the photochemical reaction with M band light was investigated as a function of temperature. Combining these two experiments with a quantitative analysis of dichroism both in the F and M bands, it is concluded that the M centre is one-electron centre, that the 2nd M band exists in the F band region, that the absorption considered to be a continuum of the M centre exists in the short wavelength branch of the F band and that the oscillator strength of the M main band is assigned to 0.83. The reciprocal of the quantum yield of the M centre is expressed by $1 + 1.4 \cdot 10^{-7} \exp(0.50/kT)$ for kT in ev. It is also concluded that the R centre has its another absorption in the spectral region of the F band.

§ 1. Introduction

Ottmer¹⁾ has first discovered the M absorption band beside the F band and carried out the experiment both with absorption measurements and with photoelectric effect in the M band of NaCl and KCl crystals coloured with X-ray. However, the systematic and more detailed experiment was made later since 1940 by Molnar* and St. Petroff²⁾, independently.

* J. P. Molnar: The article quoted in the reference by F. Seitz.⁴⁾

Göttingen school studied this subject on the crystal of KCl coloured additively. Firstly, St. Petroff showed that the F centres are converted into the A, B, C(M), D(R_2), E(R_1) and G(N) centres when the specimen containing only F centres was illuminated with light lying in the F band, and made a detailed experiment on the relationship between these centres ranging from -170°C to above 100°C . Except for the B centre, these so called *complex centres* are detected as the well defined

absorption bands on the red side of the F absorption band (see, Fig. 2(b)). One of the characteristic features of this photochemical reaction is that these photochemical products are created simultaneously accompanying an ionic motion during the course of photochemical reaction with F band light. (see, Fig. 2(a)). This reaction is quite contrasted with the F to F' or the F' to F transformation which is characterized by the pure electronic processes in a crystalline and photon field. Secondly, Barth³⁾ examined the photoconductivity in the spectral region of the M band from -150°C to near 30°C . He found that the quantum yield for the production of the photoelectric current of the M centre is nearly equal to one tenth of that of the F centre at room temperature, although Ottmer could not detect any contributions of the M centre to the photocurrent, because of its small concentration in his specimen, presumably.

Seitz⁴⁾ proposed tentatively the atomic model of the M centre which is consisted of one F centre and a pair of vacancy attached to it. Some modification of this model is made recently by Knox,⁵⁾ on the basis of the experiment on the Stark effect of the M centre by Overhauser and Rüdhardt,⁶⁾ indicating that the M centre has no permanent dipolemoment and thus it should have an inversion symmetry.

These models have a common feature that the M centre is one electron carrier and that the optical dipolemoment is parallel to the $\langle 110 \rangle$ of the crystal. In fact, the M band shows strong dichroism when it was illuminated with light polarized along the $\langle 110 \rangle$ in this band at room temperature.⁷⁾⁻¹¹⁾ This fact indicates that the M centre may have such a structure as the Seitz or Knox model. However, dichroism of the M band may be induced even when the dipolemoment is directed to the $\langle 111 \rangle$ of the crystal. From the experimental point of view, moreover, it is not so evident that the M centre carries one electron. It was discovered by van Doorn that the F band also shows dichroism when it was illuminated with light polarized along the $\langle 110 \rangle$ in this band at the presence of the M band, and thus, he proposed another model of the M centre which consists of two F centres and has the second absorption band in the spectral

region of the F band.¹²⁾ These models are shown in Fig. 1.

In connexions with these experiments, luminescence of the F and M bands and its polarization analyses have been made hitherto.⁸⁾¹⁰⁾¹²⁾¹⁴⁾ Presently, there are two possibilities to interpret the phenomena: (i) energy transfer mechanism between F and M centres, and (ii) the second absorption band of the M centre hidden in the F band.

Thus, it is desired to decide which of these models may correspond to experimental facts. Up to the present, the number of F centres corresponding to one M centre is not known except for a few experiment.¹⁰⁾¹³⁾ This may possibly be due to the fact that the A, M, R and N centres are simultaneously constructed by illumination with F band light at room temperature. Recently, it is noticed that the A, R and N centres are thermally transformed into F centres in the temperature range between 50°C and 130°C , and that the M centre is thermally the most stable among

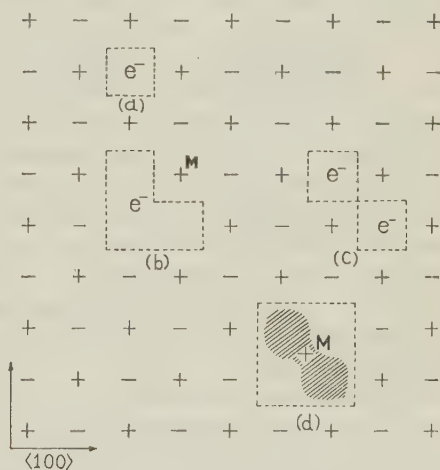


Fig. 1. A schematic representation of atomic models of colour centres. +: a positive ion, -: a negative ion, and e^- : an electron. (a): de Boer model of the F centre. (b): Seitz model of the M centre. (c): van Doorn model of the M centre. (d): Knox model of the M centre. In this case, the positive ion marked with M is situated at the midway between the positive ion vacancy and the positive ion marked with M in (b). The electron trapped in this box makes the central pair of electron-ion M whose possible distribution is distorted toward the nearest neighbouring positive ions, as indicated by the shaded region.

photochemical products and decomposes into the F centre above 130°C. These facts enabled us to determine the number of the F centre which is required to form one M centre. The problem of this work is to determine experimentally the followings:—

- (1) The thermal behaviour of the complex centres,
 - (2) The dissociation energies of the M, R and N centres,
- and
- (3) The number of the electron in the M centre.

The consideration is also given as to the possible configuration of the M centre. The preliminary account of the results was already reported.¹⁹⁾²²⁾

§2. Experimental Procedure

The specimen employed in this experiment was the synthetic single crystal of KCl grown from the melt in a platinum crucible and coloured additively heating it in the vapour of potassium. The fresh coloured crystal showed only the F band accompanied with a trace of the M band. The desired temperature of the specimen was obtained by the vegetable oil heated by an electric current through the nichrome wire (500 W) immersed in it, and the temperature was registered by the Copper-Constantan thermocouple inserted into the copper block in which the specimen was held. The whole system was shielded thermally by a dual vessel evacuated to 10^{-5} mmHg. The constancy of the temperature during the experiment was possible to retain within the accuracy of $\pm 1^\circ\text{C}$.

The optical measurements were made with use of a reference uncoloured crystal to eliminate the reflection loss on the surface of the specimen, unless otherwise described. The spectrophotometer, the Model Hitachi EPB-U, covers the wavelength range from 350 m μ to 1,000 m μ .

§3. Photochemical Reactions by Illumination with F Band Light

At room temperature, the A, M, R₁, R₂ and N centres are created simultaneously when the crystal containing only F centres was exposed to light lying in the F band, as stated in §1²³⁾. This photochemical reaction settled down to the equilibrium state at the

prolonged irradiation with F band light. Fig. 2(a) is one of the representative results which shows the variation of the absorption maxima of these bands as the illumination period proceeded at 15°C, here the incident light is monochromatic green light ($\lambda=545\text{ m}\mu$, band pass=20 m μ) and its photon intensity is the order of $1.2\cdot 10^{14}$ quanta per sec. per cm². Near the maximum of the developing curve (die Entwicklungskurve) of the A band ($\lambda_{max}=620\text{ m}\mu$, the half width=0.20 ev at 10°C), anomaly is detected on the bleaching curve of the F band. It was interpreted by St. Petroff that the anomaly is responsible for the progenitor of the M centre, *i. e.*, the B centre. The curve 2 in Fig. 2(b) shows the absorption spectrum at the time when the A band reached its maximum height of the developing curve in Fig. 2(a). The A band is easily detected as a well defined band by the difference measurement. A subsequent decrease of the absorption maximum of the A band is caused mainly by the decrease of the F band on which the former overlaps. On the other hand, it is not detected any anomaly on the bleaching curve of the F band even when the M band is lowered at a later

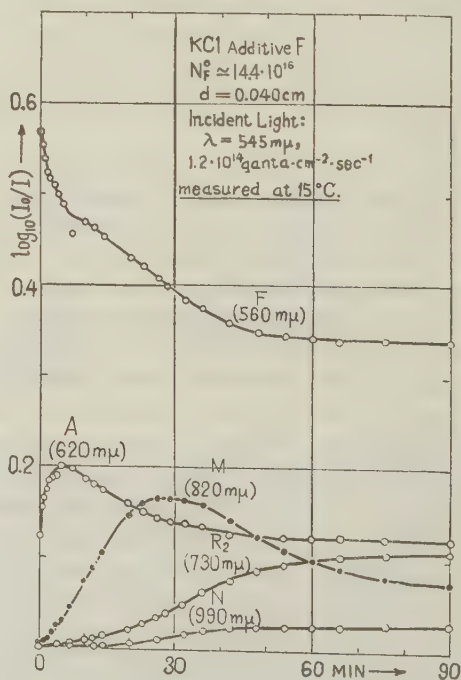


Fig. 2 (a): Variation of the absorption maxima of the F, A, M, R₂ and N bands when the photochemical reaction with F band light proceeded at 15°C.

stage of illumination with F band light. The curve II in Fig. 2(b) represents the spectrum at the stage when the M-curve reached its maximum height. The bleaching curve for the F band is re-examined in relation to the developing curve for A, M and R bands in §8. At the illumination period of 140 min., five curves become parallel to the abscissa of the figure. This corresponds to the equilibrium state at 15°C. The absorption spectrum at this instant are shown by curve 3 in Fig. 2(b). Usually, it is detected that the K band and the short wavelength branch of the F band are enhanced with this reaction (see, §7).

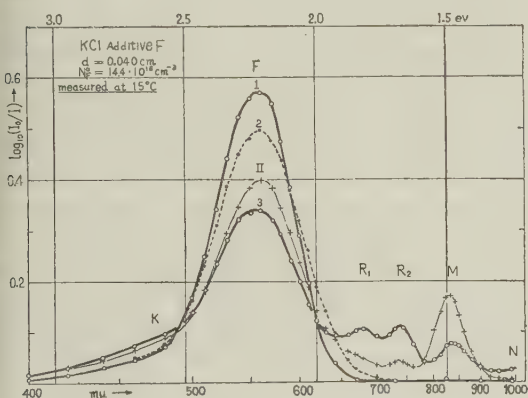


Fig. 2(b): The curve 1 shows the absorption spectrum for the initial state of the specimen, the curve 2 for the state at which the A-curve in Fig. 2(a) reached its maximum height, the curve II for the state when the M-curve reached its maximum height and the curve 3 for the equilibrium state at 15°C. The half width of the F band varies with the photochemical reaction.

In a crystal of KCl, these reactions are quite sensitive to the temperature at which they were carried out, and this type of the reaction is confined in a relatively narrow temperature range: When the specimen was exposed to F band light below -80°C , F' centres were created instead of the R, M and N centres^{23,24}; above the temperature of -50°C , it is sure that the photochemical reaction proceeded in the form shown in Fig. 2(a) and (b). It is observed that the ratio of the number of M centres, which is calculated with the Smakula's equation, to that of the F centre at the time when the M-curve reached its maximum height becomes smaller and the equilibrium state is settled down in

the shorter time with the rise of temperature at which photochemical reaction is measured. However, in the temperature range between

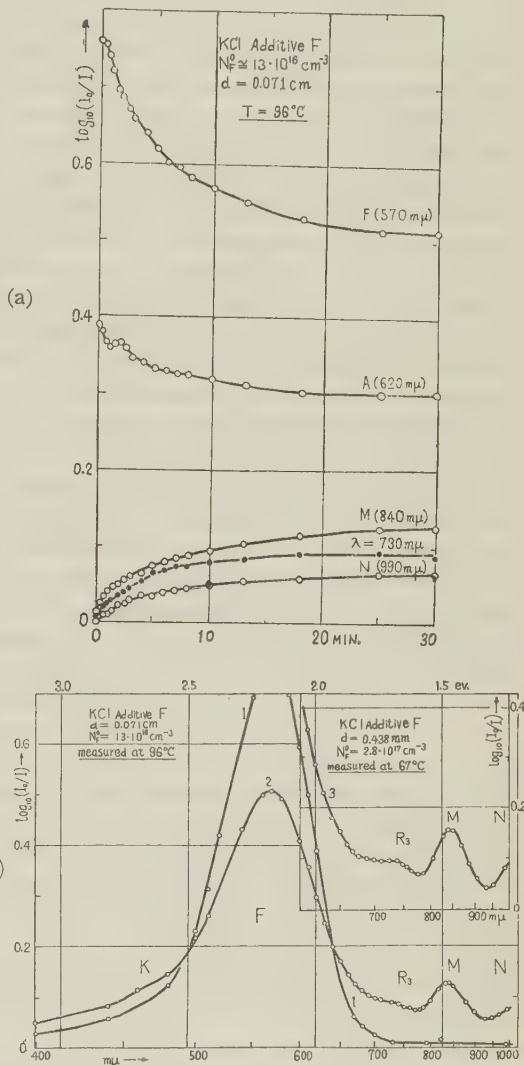


Fig. 3. (a): Variation of the absorption maxima of the F, A, M, N and that of $\lambda=730\text{m}\mu$ when the photochemical reaction with F band light proceeded at 96°C . It is noticed that the absorption maximum of the M band increases monotonously with period of irradiation with F band light. This type of variation is observed above 60°C . (b): The curve 1 is the absorption spectrum for the initial state, the curve 2 is for the equilibrium state at 96°C and the curve 3 is the absorption spectrum of the crystal which was attached to the heat reservoir kept at 67°C after the development of the R₁, R₂, M and N bands at room temperature. The photochemical products in the temperature range between 60°C and 100°C were A, R₃, M and N centres.

60°C and 100°C, it was impossible to detect the R_1 and R_2 bands when the crystal was illuminated with F band light, because of the short life time of these centres (cf. §4). Fig. 3(a) shows the variation of the absorption maxima of the F, A, M and N bands together with that of $\lambda=730\text{ m}\mu$ as the period of F band light illumination at 96°C increased. The curve 2 in Fig. 3(b) is the absorption spectrum at the equilibrium state at this temperature. The increment of the absorption between the F (or A) and the M band is not caused by the R_1 and R_2 bands, but is caused by the other kind of complex centres. In the following, we term this the R_3 , for brevity. It may well be corresponded to the R' centre designated by Scott and his coworkers.⁴⁾ The statement that the R_3 differs from the R_1 and R_2 is based upon the following facts:

(1) After the R_1 and R_2 centres (together with the A, M and N centres, of course) had been created with the consumption of the F centres at room temperature, this crystal was heated slowly up to the temperature of 60°C, for example. Then, the R_1 and R_2 centres dissociate thermally into the other centres (see, Fig. 5). The decay rate of the absorption at $\lambda=730\text{ m}\mu$ suffers a sudden change whenever the absorption spectra between the F and M bands change its shape into the one shown in Fig. 3(b) (the curve 2 or 3).

(2) Even when the crystal showing the R_3 band was cooled slowly to room temperature,

little change could be observed in the shape of the absorption spectrum between the F and M bands, and the two peaks corresponding to the R_1 and R_2 bands were not resolved.

Thus, above 60°C, the photochemical reaction with F band light is slightly different from those at room temperature. The photochemical products are the R_3 , M, N and A centres in the temperature range between 60°C and 100°C. The R_3 centre is also thermally unstable above 100°C.

The A and N centres can exist stably up to the temperature near 100°C. The most stable product is the M centre which dissociates thermally above 130°C. Therefore, the photochemical reaction with F band light has another aspect above 130°C. When the crystal of KCl containing only F centres is irradiated with light in the F band at 165°C where the pure M centres are thermally unstable, a broad band lying on the red side of the F band appears together with the M band which is detected as a small hump whose peak is located at 850 m μ . If these products are cooled to room temperature, a weak peak is observed at 670 m μ beside the one at 820 m μ . The latter is considered to correspond to the M band, and the former may presumably be ascribed to the higher aggregates of F centres. These phenomena are illustrated in Fig. 4.

Above 200°C, the detailed experiments were carried out mainly by Scott and his coworkers.¹⁵⁾¹⁶⁾¹⁷⁾

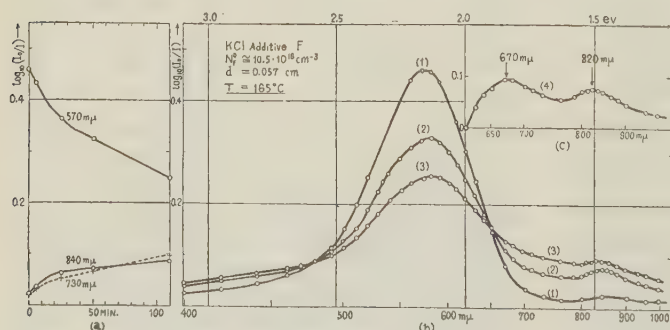


Fig. 4. The photochemical reaction with F band light at 165°C.

(a): Variation of the absorption maxima of F and M bands with period of illumination with F band light. (b): The curve 1 is the absorption spectrum for the initial state of the specimen, the curve 2 and 3 correspond to spectra when the crystal was illuminated with F band light for 50 and 110 min at 165°C, respectively, and the curve 4 is the difference of the curve 3 and the initial state both measured at 20°C.

§4. Thermochemical Reactions of Complex Centres

In the analysis of thermochemical reactions, it is the most important problem to decide the order of the reaction. The answer of this basic problem is, of course, not obvious, *a priori*, even in the case of reaction of colour centres, because it depends upon the nature of the process. If a colour centre decays thermally in the form of the first order, the concentration N per cm³ at the time t sec is expressed by the logarithmic law:

$$N = N_0 \cdot \exp(-t/\tau), \quad (1)$$

where N_0 is the concentration at $t=0$, and τ is a relaxation time for the dissociation process at a given

temperature. In the first and the second order of the reaction, τ is expressed by the Arrhenius equation:

$$1/\tau = B_0 \cdot \exp(-E/kT), \quad (2)$$

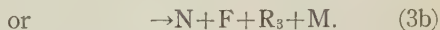
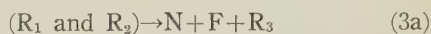
where B_0 is a constant corresponding to the frequency factor of the process, E an activation energy of the process, and k the Boltzmann constant.

Generally, the rate with which a thermochemical reaction takes place is very sensitive to the thermal history of the specimen. For example, when dichroism was induced in the M band by illuminating with light in this band polarized along the $\langle 110 \rangle$ at a higher temperature, say at 90°C , it is observed that the thermal reorientation of the M centre in its ground state takes place in the dark in the direction that the induced dichroism vanishes. In this case, the amount of dichroism decreases satisfying the logarithmic law.¹¹⁾ When the specimen was heated above 90°C and subsequently cooled to this temperature prior to exposure to M band light, on the other hand, it is usually observed that dichroism of such a specimen vanishes thermally showing a departure from the logarithmic law, or decreases with a too larger value of the relaxation time to be expected at 90°C ,

even if the logarithmic law is satisfied. The phenomena sensitive to the thermal treatment were also observed in the thermal decomposition of R centres.

When the crystal containing the F, M, R and N centres is heated slowly to the temperature above 50°C , R centres dissociate thermally according to the logarithmic law so long as the absorption spectra show the two peaks of R_1 and R_2 bands. This is shown in Fig. 5(a). When these two peaks smeared out into the R_3 band, however, the thermal decay at $730\text{ m}\mu$ takes place more slowly. Alternatively, when the crystal containing a considerable amount of the R_1 and R_2 centres was directly attached to the heat reservoir kept at the temperature of 50°C , for example, the decay of the absorption constant at $730\text{ m}\mu$ took place deviating from the logarithmic law and the R_3 band appeared in the shorter time. The behaviour of the thermochemical reaction is shown by Fig. 5(b) and the final state is represented by the curve 3 in Fig. 3(b).

In spite of these complexities, it is possible to state that the thermochemical reaction takes place in the next form in the temperature range between 50°C and 100°C :



The (3a) reaction is usually observed on the specimen in which the M band was developed up to near M_{max} of the M-curve of Fig. 2(a) at room temperature, and the (3b) is on the specimen to which F band light was exposed until a photochemical equilibrium state was settled down.

By this reaction, the N band was remarkably enhanced to height which could never be attained by illumination with F band light at room temperature. This is illustrated by Fig. 6. The curve (1) is the spectrum corresponding to an equilibrium state of a photochemical reaction with F band light at room temperature, and the curve (2) is the one measured at room temperature after the reaction (3) completed. The N center was hardly bleached by illumination with light in this band over the entire temperature range where it is stable

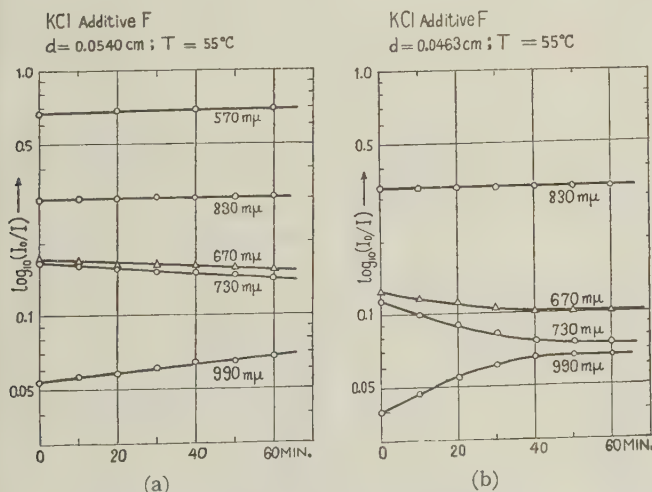


Fig. 5. The thermochemical reaction at 55°C .

(a): The specimen was heated slowly up to 55°C after the R band had been developed at room temperature to the linear part of the R-curve in Fig. 2(a). The decay of the R band takes place satisfying the logarithmic law. (b): The specimen was attached directly to the heat reservoir kept at 55°C after the R band had been developed under the same condition as that of (a). The decay takes place deviating from the logarithmic law.

thermally. When the specimen which underwent the reaction (3) was exposed to F band light at room temperature, however, the spectrum (1) reappears at the prolonged illumination and, thus, the equilibrium state of the photochemical reaction with F band light is again established. In another word, the N centres are easily destroyed with F band light. This is quite similar to the phenomenon that the photochemical equilibrium state between F and F' centres at a given temperature was easily destroyed by exposure to X-ray at another temperature.²⁰⁾ The N centres were also destructed effectively by illumination with light in the R₃ band ($\lambda_{max} = 720\text{ m}\mu$ at 15°C), and R₁ and R₂ bands reappeared. This is shown by the curve (3). It is convinced that these properties will be worthy of special attentions.

The determination of the relaxation time τ for the dissociation process of the R centre was less reliable because of the simultaneous creation of the R₃ band at the same position as that of the peak of the R₂ band on the one

hand, and of the effect of the red tail of the F band modified with the A band on the other hand. The latter prevented us from the difference measurement. However, τ of the reaction was determined formally by taking the inclination of the decay curve of Fig. 5 (a) in order to clarify the temperature range in which the R₁ and R₂ centres decompose thermally with a measurable frequency. This was shown in Fig. 8. The measured points were rather distributive, and the line drawn tentatively gave the frequency factor in Eq.

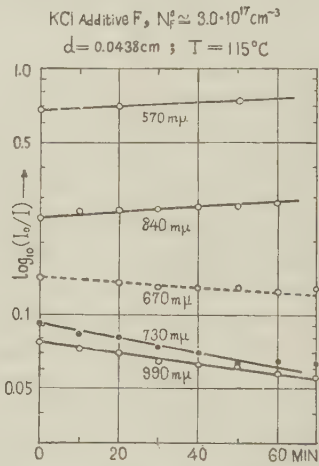


Fig. 7. The thermochemical reaction (4) at 115°C.

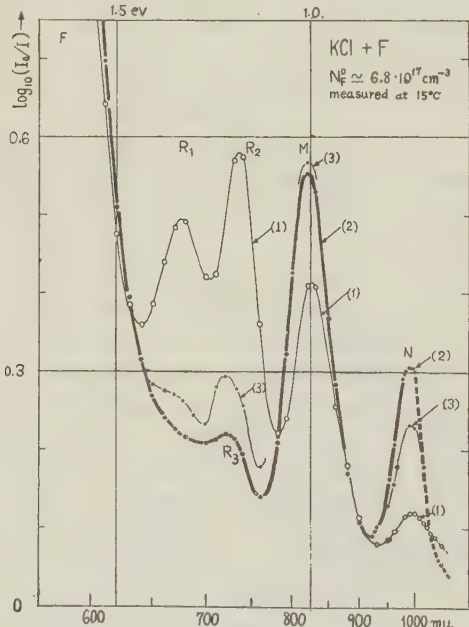


Fig. 6. The thermochemical reaction (3) and the photochemical reaction with R₃ band light, (see the text).
(1): The initial state of the reaction (3),
(2): The final state of the reaction (3) measured at 15°C,
(3): The photochemical reaction with R₃ band light at 15°C.

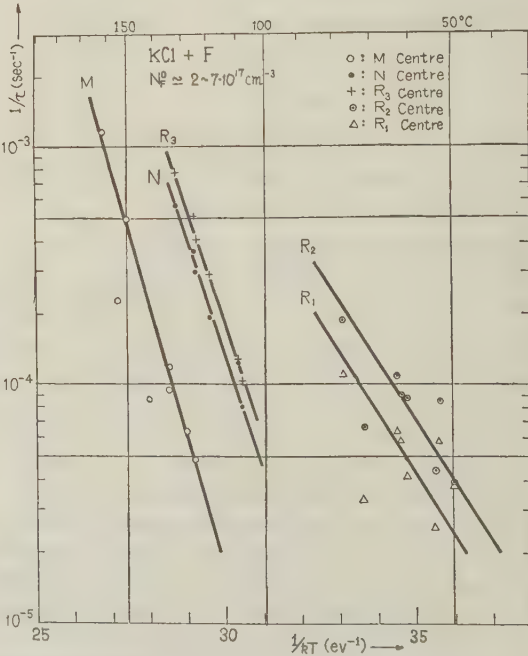


Fig. 8. The reciprocals of τ for the complex centres plotted against $1/kT$ (in ev^{-1}), (see the text).

(2) the value of the order of $4.7 \cdot 10^4 \text{ sec}^{-1}$ and the activation energy of 0.6 eV,

The N and R_3 centres decompose thermally into the F and M centres above 100°C :



The reaction (4) satisfies the logarithmic law, as shown in Fig. 7. For $1/\tau$ of the reaction, the measured points were also plotted in Fig. 8 and were expressed by the next equations:

$$\text{N: } 1/\tau = 3.98 \cdot 10^{10} \exp(-1.11/kT) \text{ sec}^{-1}, \quad (5a)$$

$$R_3: 1/\tau = 7.96 \cdot 10^{10} \exp(-1.12/kT) \text{ sec}^{-1}. \quad (5b)$$

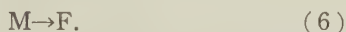
for kT in eV.

Thus, we have the next relation:

$$2(1/\tau)_N \cong (1/\tau)_{R_3}. \quad (5c)$$

It is possible to realize the condition that the specimen contains only F and M centres, by the reaction (4).

Above 130°C , M centres return thermally to F centres according to the logarithmic law:



When the specimen was cooled to room temperature after the reaction (6) had been over, the absorption spectrum recovers the initial state within experimental errors. The reciprocals of τ of the reaction (6) were plotted as a function of $1/kT$ in Fig. 8. They are expressed by the next equation:

$$1/\tau = 2.01 \cdot 10^{12} \exp(-1.31/kT) \text{ sec}^{-1}.$$

$$\text{for } kT \text{ in eV.} \quad (7)$$

In this case, the rate of the reaction (6) was also quite sensitive to the thermal history of the specimen and to the presence of a trace of the other centres, such as N or R_3 remained.

The relation (7) implies that electrons ejected from the ground state of the M centres into the conduction band by thermal agitations are eventually captured by Cl^- vacancies to form F centres.

§ 5. The Oscillator Strength of the M Band

In the preceding paragraph, the thermal stability of the photochemical products in an additively coloured KCl crystal was studied quantitatively. Fig. 8 summarized the results and illustrated the temperature ranges in which they decompose thermally with a measurable frequency. From these experiments, two facts are obtained: (i) The M centre is

thermally the most stable among the photochemical products; (ii) when the crystal containing F, A, R, M and N centres was heated to destroy the photochemical products thermally and subsequently cooled again to room temperature, the absorption spectra recover to the original F band within experimental error. The above two facts enable us to determine the number of the F centre corresponding to one M centre with high precision.¹⁹⁾ At room temperature, the M centres are created by the consumption of F centres. However, the number of destructed F centres does not directly correspond to that of the created M centres owing to the simultaneous photochemical reaction as stated in §3 (cf. §8, too); alternatively, when the KCl crystal containing F centres together with the A, R, M and N centres is heated from room temperature to the higher so as to decompose the complex centres except for the M centre, the number of decreased F centres should be equal to that of M centres remained, under the assumption that the M centre carries only one electron. The experiment in this section was carried out on this principle.

After the KCl crystal containing only F centres had been illuminated with light in the F band at room temperature to produce sufficient amount of M centres, it was heated slowly up to 115°C and subsequently cooled once again slowly to room temperature. With use of this procedure, it was possible to decompose A centres and a small amount of R and N centres almost completely into F centres leaving only M centres. Fig. 9 demonstrates this clearly. In Fig. 9 (a), the crystal was illuminated with light in the F band until a photochemical reaction reached its equilibrium state at 20°C . In this case, it was necessary to heat the crystal to 138°C in order to decompose the N centre completely. The absorption spectra were measured using the difference method owing to the high concentration of F centres. Since the spectrum corresponding to the initial state is to be represented by $\Delta A = 0$, where ΔA is the relative optical density, Fig. 9 (a) shows directly the absorption area of the decreased F centres (the shaded region) and that of the constructed M centres at the cost of the former. It is, however, observed that the K band and the short wavelength branch of the F band are en-

hanced. In Fig. 9 (b), the coloured crystal was illuminated with F band light for 20 min at 20°C (cf. Fig. 2 (a)). The curve 1 is the absorption spectrum of the initial state at 20°C, the curve 2 is that of the specimen heated to 115°C after the development of the M band at room temperature and subsequently cooled to 20°C, and the curve 3 is the increment of the optical absorption in the spectral region except the M band. They show that the necessary condition for obtaining the oscillator strength of the M band, *i.e.*, the crystal contains only F and M centres, is

satisfied except for the small increase of the short wavelength branch of the F band.

Now, the number of the F centre ΔN_F per cm^3 which was consumed in the construction of M centres is easily calculated by the Kleinschrod-Smakula's equation²⁰:

$$\Delta N_F = 1.31 \cdot 10^{16} H_F \cdot \Delta K_F, \quad (8)$$

where

H_F = The half width of the F band,

and

ΔK_F = The variation of the maximum absorption constant of the F band.

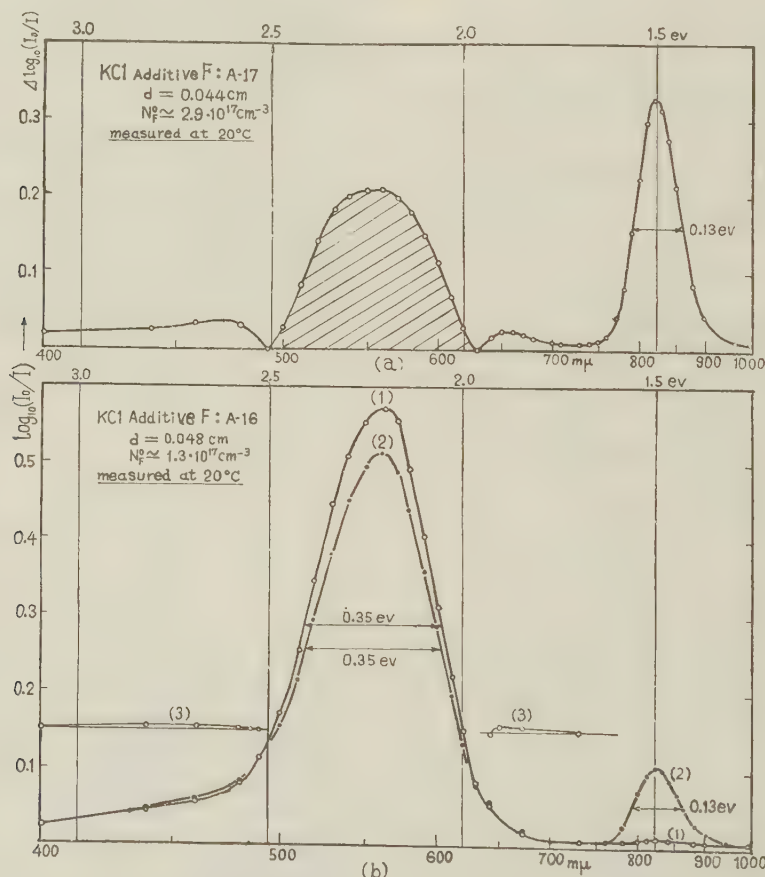


Fig. 9 (a) and (b). The absorption spectra of the specimen which contains only F and M centres. The small amount of increment of absorption near 650 μm is due to the residual A band.

(a): The absorption spectrum measured with a difference method. The shaded region represents the absorption area of the decreased F band, and the remainder for the increment of the absorption spectra at the cost of the F band. The specimen was heated to 138°C after exposure to F band light at 20°C and was subsequently cooled to 20°C.

(b): The curve 1 is the absorption spectrum of the initial state of the specimen at 20°C, the curve 2 is the one that was heated to 115°C after exposure to F band light for 20 min at 20°C and was subsequently cooled to 20°C, and the curve 3 is the increment of the absorption in the spectral region except for the M band.

Table I. Experimental Values of the Ratio $R = -\Delta N_F / (f_M \cdot N_M)$ measured at 20°C.

Specimen	Original density of F centres N_F (cm ⁻³)	Consumed F centres $-\Delta N_F$ (cm ⁻³)	Created M centred $\Delta(f_M N_M)$ (cm ⁻³)	Ratio $ R $
A-17 (0-3)†	$2.9 \cdot 10^{17}$	$4.95 \cdot 10^{16}$	$2.57 \cdot 10^{16}$	1.93
A-16 (III-5)§	1.3	1.26	0.64	1.98
A-18 (III-5)	1.3	1.73	0.83	2.08
A-20 (III-5)	1.2	0.55	0.34	1.60
A-23 (III-6)††	1.4	2.25	1.04	2.17

† Fig. 9 (a), § Fig. 9 (b)

†† Measured at 125°C.

The Mean Value of $|R|$
 $= 1.95 \pm 0.22$

The number of created M centres ΔN_M per cm³ is calculated with the Smakula's equation²¹):

$$f_M \cdot \Delta N_M = 1.06 \cdot 10^{16} H_M \cdot \Delta K_M, \quad (9)$$

where

f_M = The oscillator strength of the M band

H_M = The half width of the M band, and

ΔK_M = The variation of the maximum absorption constant of the M band.

The experimental values are listed in Table I. Thus, we can obtain the relation:

$$-\Delta N_F / \Delta(f_M \cdot N_M) = 2.0. \quad (10)$$

This leads to the relation $f_M = 0.5$, if the M centre carries one electron and has a cubic symmetry as the F centre. The experiment in the next paragraph may decide the validity of the former assumption. However, the latter is not valid, because the experiment upon dichroism of the M band shows that the optical dipolemoment of the M centre is directed to the special crystallographic direction except for the $\langle 100 \rangle$ of the crystal. Hence, the obtained value 0.5 is but formal.

It is generally known well that the half width of the F band becomes wider when the F band was illuminated with light in this band. For example, at 15°C the half width of the F band is 0.34 eV at the initial state, 0.38 eV at the stage of A_{max} of the A-curve, 0.36 eV at M_{max} of the M-curve and finally 0.38 eV at a photochemical equilibrium state as seen in Figs. 2 (a) and (b). This variation of the half width should not directly be connected with the presence of the other band of the M centre hidden in the F absorption, but is ascribed certainly to the overlap of the A and R bands with the F band, because the half width of the F band is

kept at a constant value 0.35 eV irrespective of the presence of the M band, or it becomes slightly smaller than that of the original one as shown in Fig. 9 (b). Thus, it is safely concluded that the second absorption band of the M centre does not affect the half width of the F band, even if the former should exist and happens to superpose with the latter.

In the determination of a ratio $-\Delta N_F / \Delta(f_M \cdot N_M)$, any correction was not made concerning the increment of the absorption area in the short wavelength branch of the F band. It is proved in § 7 that this is of no need.

§ 6. The Quantum Yield of the Photochemical Reaction with M Band Light²²)

When the M band developed at 20°C was illuminated with light in the M band at a given temperature, the electrons ejected from the M centres are captured in the trap forming other centres which are stable thermally at this temperature, *i.e.*, F, R and N centres below 50°C, the F and N (and R_3) centres between 100°C, and 50°C, and F centres above 130°C. Generally, the amount of the photochemical products except the F centre is exceedingly smaller than that of those with light in the F band.

In the photochemical reaction:



the quantum yields η_F and η_M were defined by the next equations:

$$\left. \begin{aligned} \eta_F &= \partial N_F / \partial q_M, \\ \eta_M &= \partial (f_M N_M) / \partial q_M, \end{aligned} \right\} \text{ at } q_M = 0 \quad (12)$$

$$(13)$$

where ΔN_F and $\Delta(f_M N_M)$ were calculated with eqs. (8) and (9), respectively, and the quanta absorbed in the M band are denoted by q_M .

As a preliminary experiment for checking the photon intensity, which was measured with the calibrated thermopile of Kipp, the quantum yield for the conversion of F to F' was measured as a function of temperature. The results are represented in Fig. 10, where the points measured by Pick¹⁸⁾ and by the present author are marked with + and o, respectively. The agreement between them is fairly satisfactory.

As an example of the photochemical reactions with light in the M band, ΔN_F and $-\Delta(f_M N_M)$ were plotted as a function of light

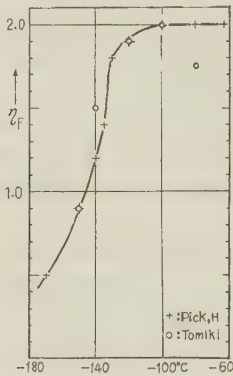


Fig. 10. Experimental confirmation of the photon intensity with use of the well defined F to F' transformation. η_F is the quantum yield for this reaction.

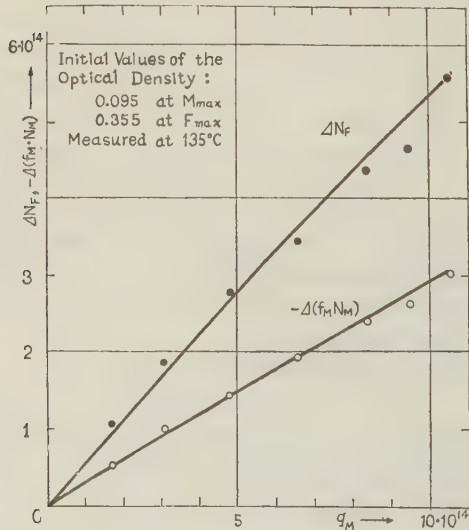


Fig. 11. The photochemical reaction with light in the M band at 135°C. ΔN_F and $-\Delta(f_M N_M)$ are plotted against the quanta absorbed in the M band q_M . In this case, $\eta_F = -2\eta_M = 0.56$.

quanta absorbed in the M band at 135°C in Fig. 11. The experimental values of η_F and η_M were plotted in Fig. 12 as a function of temperature, where η_M is marked with o and η_F with +. It is clearly observed that both η_F and η_M reach the maximum value above 130°C and that there exists a definite relation:

$$\left. \begin{aligned} \eta_F &= -2\eta_M, \\ \eta_F &= 0.56 \pm 0.050. \end{aligned} \right\} \text{above } 130^\circ\text{C}$$

(14a)

(14b)

The equation (14a) ascertains that all the electrons departed from M centres are solely captured in Cl⁻ vacancies to form F centres in the temperature range where M centres decompose thermally into Fcentre s*) (cf. Eq. (10)). Then, one may interpret Eq. (14b) in a way that the M centre carries one electron at most. In the following, the descriptions were made on this basis.

Now, Eq. (14b) indicates that one of two

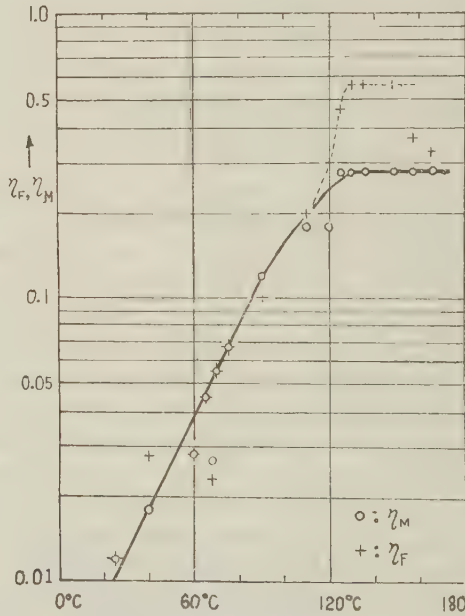


Fig. 12. The quantum yield η_F and η_M in the reaction with light in the M band are plotted against temperature.

*) The contribution of the thermally decomposed M centres to η_F and η_M can be neglected so long as $A_{M,max} \simeq 0.10$ at $q_M = 0$, because the number of electrons ejected from M centres by absorption of photon energy is exceedingly larger than that of those by thermal agitations, i. e., a series of measurements of the specimen is completed within five minutes or so, on the other hand the M centre decomposes thermally according to Eq. (5).

electrons ejected from M centres by absorption of two photons is captured in the Cl^- vacancy to form an F centre and the other in another trapping centre to form an M centre. However, it was rather surprising that the latter can fix an electron in the conduction band as firmly as the Cl^- vacancy in the circumstance that it frees an electron thermally.

Now, if the optical dipolemoment of the M centre is parallel to the $\langle 110 \rangle$ of the crystal, one third of $6N_0$ dipolemoments shall be detected optically, where N_0 is the concentration of the M centre per cm^3 which is parallel to one of the $\langle 110 \rangle$. Therefore, Eq. (10) indicates that f_M should be greater than unity, i.e., $f_M=1.5$. This is quite contradicted to the another experimental fact $\eta_F=0.56$ on which basis it has been interpreted that the M centre carries only one electron at most. However, if we postulate the second absorption band of the M centre in the spectral region of the F band, the paradox stated above is removed. This is described below:

If it is assumed that the second absorption band of the M centre happens to overlap with the F band, the optically detected decrement $-dN_F$ should be multiplied with the overlapping factor p in order to obtain the net variation of the concentration of the F centre. p is obtainable under the requirement that the net quantum yield of the F centre η_F^* should be unity above 130°C where the M centre decomposes thermally into the F centre:

$$\eta_F^* = \partial(p \cdot N_F) / \partial q_M = 1.0. \quad (15)$$

With use of Eq. (14b), we have

$$p = 1 / (\partial N_F / \partial q_M) = 1 / 0.56 = 1.8. \quad (16)$$

The results (10) and (16) indicate that the height of the second absorption band of the M centre is equal to one half of that of the main band.

Now, it is easy to calculate the oscillator strength of the M band. We denote by f_{Mj} the oscillator strength of the j -th band and by $f_{M\infty}$ the oscillator strength of the continuous absorption of the M centre. If it is assumed that the optical dipolemoment is directed along the $\langle 110 \rangle$ of the crystal as in the Seitz-Knox model, the relation (10) is written in the next form:

$$\Delta(p \cdot N_F) / \Delta(f_{M1} \cdot 2N_0) = -2p,$$

where N_0 is the concentration of the M center per cm^3 directed along one of the $\langle 110 \rangle$. With using of the relation:

$$\Delta(p \cdot N_F) = -\Delta(6N_0),$$

we have

$$f_{M1} = 3 / (2p) = 0.83, \quad (17)$$

and from the f -Sum rule

$$\sum_{j=2}^{\infty} f_{Mj} = 1 - f_{M1} = 0.17. \quad (18)$$

The accuracy of the results (14), (17) and (18) is within the order of $\pm 10\%$.

To proceed with an analysis further, it is adequate to introduce the quantity η_M^* , the net quantum yield of the M centre, and derive the relation connecting η_M^* to η_M . Prior to exposure to M band light, the specimen is certainly isotropic in the sense that the M centres are distributed with equal concentration along the possible independent orientations. This state of the uniform distribution is destroyed inevitably during the course of the photochemical reaction with M band light. Then, the quantum yield η_M defined by Eq. (13) should be expressed in the next form:

$$\eta_M = -f_{M1} \cdot \partial(N_s + N_D) / \partial q_M \quad \text{at } q_M = 0,$$

where N_D and N_s are the concentration of the M centre along one of the $\langle 110 \rangle$ on the $\{100\}$ which are parallel and normal to the propagating direction of incident light, respectively. We define the net quantum yield η_M^* by

$$\eta_M^* \equiv -\partial(\text{Total Number of the M Centre}) / \partial q_M \quad \left. \vphantom{\eta_M^*} \right\} \\ = -\partial(2N_s + 4N_D) / \partial q_M.$$

at $q_M = 0$

Then, we have the relation:

$$\eta_M^* = 3 \frac{\eta_M}{f_{M1}} - \left\{ -\frac{\partial}{\partial q_M} (N_D - N_s) \right\}_{q_M=0}.$$

At the higher temperature ($>80 \sim 100^\circ\text{C}$), the thermal reorientation of the M centre in the ground state takes place so frequently that the second term of the above formula can be neglected. By exposing the specimen to M band light polarized along the $\langle 110 \rangle$, the quantity or the quantity proportional to $-\{(N_s)_\parallel - (N_s)_\perp\}$ is detected as *dichroism* in this band, where by the symbol $\parallel$ it means the concentration of the M centre parallel to the electric field of the polarized light and by $\perp$ the one normal to it. It was already confirmed experimentally that the quantity η_D is characteristic to the M band¹¹⁾, where η_D is

defined by

$$\eta_D = - \frac{\partial}{\partial q_M} \{ (N_s)_\parallel - (N_s)_\perp \} \quad \text{at } q_M = 0.$$

Usually, η_D is small compared to $3\eta_M/f_{M1}$ and is actually the order of one sixth of the latter over the entire range of temperature below 80°C. It is obvious that the quantity $-\{\partial(N_p - N_s)/\partial q_M\}_{q_M=0}$ is far smaller than η_D .

Thus, we are led finally with a sufficient accuracy to the next equation:

$$\eta_M^* = 3\eta_M/f_{M1}. \quad (19)$$

It will be worthy of mentioning here that Eqs. (17), (18) and (19) are equally valid to the model of the M centre of which dipolemoment is directed to the arbitrary $\langle hkl \rangle$ crystallographic direction.

Above the temperature of 130°C, combining Eq. (19) with (15) and (14a), we have

$$\eta_M^* = 2p \cdot \eta_M = p \cdot \eta_F = 1.0. \quad (20)$$

The postulation (15), that requires η_F^* should be equal to unity, leads to the conclusion that the quantum yield of the M centre η_M^* is also equal to unity, and furthermore the oscillator strength f_{M1} gets a value smaller than unity.

As shown in Fig. 9(b), even when the "pure" M band existed on the longer wavelength side of the F band, its half width remained unaltered from that of the F band at the initial state, and, in addition to this, any anomaly responsible for the second band of the M centre was not detected in the shape of the F band.* In order to be in concordance with these facts, the hypothetical second band of the M centre should be located in the spectral region of the absorption maximum of the F band, and its half width be equal to or smaller than that of the F band. In the next, the half width of the second M band is evaluated:

Since, in the visible region, the numerical factor of the Smakula's equation can be regarded as constant, we can put

*) It is observed that the anomaly similar to a small shoulder of the F band appears at 545 and 575 m μ , and that the half width of the F band becomes smaller than that of the initial one by 0.005 eV. It will be problematical to regard these finer deviations as the evidence of the second absorption of the M centre, because they are probably in the limit of the accuracy of the measurement by a spectrophotometer.

$$(H_{M1} \cdot \Delta K_{M1})/f_{M1} = (H_{M2} \cdot \Delta K_{M2})/f_{M2}, \quad (21)$$

where we denoted by H_{Mj} and K_{Mj} the half width and the absorption maximum of j -th band of the M centre, respectively. Under the assumption that the absorption maximum of the second M band is located at the same wavelength of that of the F band, the next equation is also valid:

$$\Delta K_{M2} \simeq (p-1) \cdot \Delta K_F. \quad (22)$$

With use of Eqs. (21), (22) and (10), we have

$$\frac{H_{M2}}{f_{M2}} = \frac{1}{2(p-1)} \cdot \frac{H_F}{f_{M1} \cdot f_F} \quad (23)$$

$$\simeq 0.32 \quad \text{at room temperature.} \quad (23a)$$

If it is assumed that f_{Mj} 's ($j \geq 3$) are vanishingly small, i.e., $f_{M2} \simeq 0.17$, then the half width of the second M band is approximately evaluated:

$$H_{M2} \simeq 0.054 \text{ eV at room temperature.} \quad (23b)$$

$$\ll H_F (\simeq 0.35 \text{ eV}).$$

Thus, the result (23b) is also consistent with the above requirement. Generally, the half width of the absorption band of a colour centre is mainly affected by the lattice vibration, and this was already confirmed earlier by Mollwo²³⁾ who found that the increment of the half width of the F band was expressed by a linear function of the specific heat of the crystal. Therefore, the half width of the second band of a colour centre is expected to be smaller than that of the first band. In this respect, the result (23b) is also satisfactory.

Now, we can calculate the net quantum yield η_M^* with use of the experimental value η_M by the relation (19). The values of η_M^* and η_F^* were plotted as a function of the reciprocal of kT (eV) in Fig. 13. The reciprocal of η_M^* is expressed by the next equation:

$$1/\eta_M^* = 1 + 1.4 \cdot 10^{-7} \exp(0.50/kT). \quad (24)$$

for kT in eV.

To attempt an interpretation of this equation, we denote by A the probability per unit time interval that the electron in the first excited state drops back to the ground state, by B the probability that the thermal agitation frees the electron and by $(1-\zeta)$ the fraction with which the electrons in the conduction band are recaptured by the trapping centre to form M centres. Then the quantum yield η_M^* is expressed by

$$\eta_M^* = \zeta B / (A + B).$$

Comparing this expression with Eq. (24), we have

$$\frac{1}{\zeta} \cdot \left(\frac{A}{B} + 1 \right) - 1 = 1.4 \cdot 10^{-7} \exp(0.50/kT).$$

At the higher temperature, ζ is nearly equal to 1, owing to the relation (14a), thus the left side of this equation can be simplified to $A/(B\zeta)$. It is shown that this holds also at sufficiently low temperature: According to the experiment upon the photoelectric effect of the M centre of a KCl crystal with 10^{17} F centres per cm^3 , $(\eta\omega/\mathcal{E})_{M,ph}$ was the order of $6 \cdot 10^{-12}$ cm per Volt/cm below -100°C ³⁾, where η is the quantum yield, ω the mean range (der Schubweg) and $\mathcal{E}$ the strength of the applied electric field, and by suffices M and ph it is denoted that the quantity is due to the photoelectric effect of the M centre; since $\omega/\mathcal{E}$ is the order of $3 \cdot 10^{-9}$ cm per Volt/cm for KCl crystal at -100°C with the same concentration of the F centre²⁴⁾, $\eta_{M,ph}$ will be the order of 10^{-3} ; thus the above expression is again reduced to $A/B(\zeta)$, because of the relations $1.4 \cdot 10^{-7} \exp(0.50/kT) \gg 1$ and $A/B \gg 1$. The above simplification is also permitted in the intermediate temperature range where $A/B \simeq 1$ is valid so long as B and ζ are defined by the equations described below. We assume here the relation $A/B(\zeta) = 1.4 \cdot 10^{-7} \exp(0.50/kT)$ to be valid in a crude approximation over the entire temperature region under considerations.

Now, we can proceed with our discussions according to the Mott and Gurney's theory²⁴⁾. If it is assumed that A corresponds to the Einstein's A coefficient, then we have

$$A \simeq 8 \cdot 10^9 (h\nu/13.54)^2 f_{M1},$$

where $h\nu \simeq 1.2 \text{ eV}$ ⁸⁾ and $f_{M1} = 0.83$. It is conceived that B will take the form:

$$B = B_{oe} \exp(-E_M/kT),$$

where E_M is the energy required to remove an electron from the first excited state of the M centre into the conduction band. It is not quite unreasonable to consider that ζ is a function of the temperature. For simplicity, we choose the expression of ζ in the next form:

$$\zeta = \zeta_o \exp(-\epsilon/kT).$$

Then, we are led to the next relations under the above approximations:

$$B_{oe} \cdot \zeta_o = 3.8 \cdot 10^{14} \text{ sec}^{-1}, \quad (26)$$

$$E_M + \epsilon = 0.50 \text{ eV}. \quad (27)$$

To determine the quantities E_M , ϵ , B_{oe} and ζ_o numerically, it will be necessary to have informations concerning the temperature dependency either of $(\eta\omega/\mathcal{E})_{ph, M}$ of the primary current or the recapture processes $(1-\zeta)$ by M centres. It appears, however, that such an experiment has not been carried out successfully up to the present.

If it is permitted to put $B_{oe} \sim 5 \cdot 10^{10} \text{ sec}^{-1}$, ζ_o has the value of $7.6 \cdot 10^3$. Then, ϵ is estimated as the order of 0.31 eV because of the relation $\zeta = 1$ at 130°C (cf. Eq. (14a)), and thus E_M is the order of 0.19 eV.

The assumption that the second M band is hidden under the F band leads to fairly plausible values for oscillator strength of the first band (Eq. (17)), quantum yield η_M^* and the half width of the second band of the M centre (Eq. (23b)).

Now, it is highly desired to detect another fact which is responsible for the hypothetical second M band hidden in the F band. This

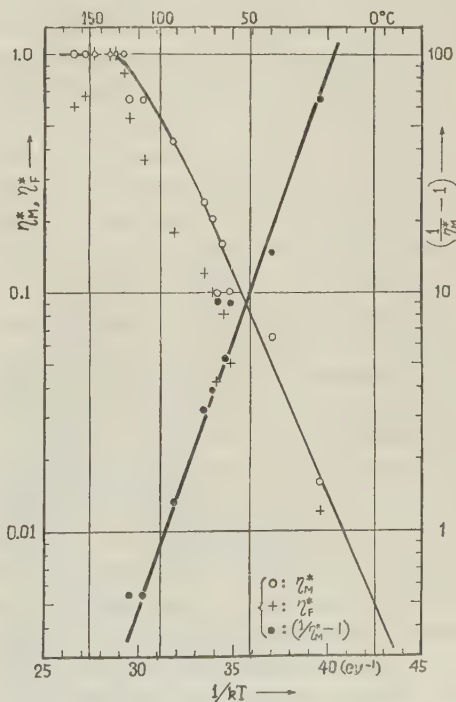


Fig. 13. The net quantum yield of the F and M centres in the photochemical reaction by M band light. The measured point at room temperature represents the mean value. +: η_F^* , $\circ$: η_M^* , $\bullet$: $(1/\eta_M^*) - 1$.

is described in the next paragraph.

§ 7. The Second M Band and Dichroism in the F Band

The hypothesis of the second band of the M centre hidden in the F band was first proposed by van Doorn¹²⁾ basing on the fact that the F band, of which centre is considered to be istoropic, exhibits dichroism when the specimen was illuminated with light in the F band polarized along the $\langle 110 \rangle$ at the presence of the M band, as stated in § 1. This hypothesis has certainly a greater advantage in the explanation of dichroism induced in the F band. However, it has a few weak point: (i) when the R band is irradiated with light in this band polarized along the $\langle 110 \rangle$, the R, F and M bands exhibit dichroism simultaneously; (ii) dichroism in the F band induced by illuminating with F or M band light polarized along the $\langle 110 \rangle$ appears on a relatively broad spectral region.

After the M band had been illuminated with light polarized along the $[110]$ in this band so as to induce dichroism in the M band (and F band) at room temperature, the F band was subsequently irradiated with light in this band polarized either along the $[110]$ or $[1\bar{1}0]$ of the crystal. Then both $A^M_{[110]}$ and $A^M_{[1\bar{1}0]}$ increased with period of illumination with F band light, where $A^M_{[110]}$ and $A^M_{[1\bar{1}0]}$ are the absorption maxima of the M band measured with light polarized along the $[110]$ and $[1\bar{1}0]$, respectively. In Fig. 14 (a), in which case the F band was irradiated with light polarized along the $[110]$ in this band, $A^M_{[110]}$ increased at an initial stage and then became constant at prolonged irradiation, while the $A^M_{[1\bar{1}0]}$ increased at first, then decreased to cross over the $A^M_{[110]}$ -curve with illuminating duration and finally became a constant value. In Fig. 14 (b), in which the direction of polarization of F band light was reversed to the $[110]$, $A^M_{[110]}$ and $A^M_{[1\bar{1}0]}$ increased and subsequently became a constant value. Two curves did not cross with each other. Thus, a part of electrons ejected from the normal state of F centres into the conduction band is captured by the trapping centre to form M centre exhibiting a strong dependency of the polarization direction of excitation light. This phenomenon is, however,

analogous to the one that the F band shows dichroism when it was illuminated with light polarized along the $\langle 110 \rangle$ in this band in its essential points. Hence, this phenomenon has the same advantage and disadvantage as the van Doorn's experiment in granting the hypothesis of the second band of the M centre. These phenomena might be interpreted either with the second band of the M centre hidden

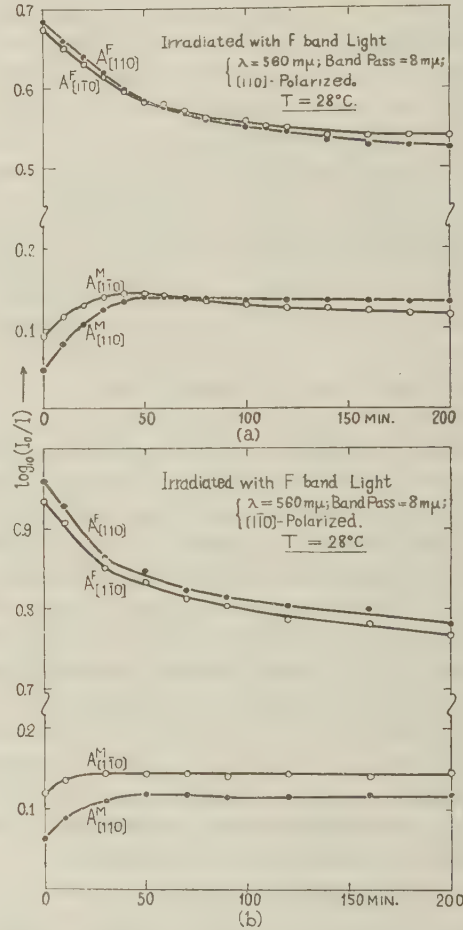


Fig. 14. Variations of absorption maxima measured with $\langle 110 \rangle$ polarized light versus the period of illumination of light polarized along the $\langle 110 \rangle$ in the F band. $A^*_{[i,j,k]}$ denotes the absorption maximum of the * band measured with light polarized along the $[i,j,k]$. (After Ishii, Tomiki and Ueta)

(a): The specimen was illuminated with light polarized along the $[110]$ in the F band after the M band had been bleached partially with light polarized along the $[110]$ in this band.

(b): The specimen was illuminated with light in the F band polarized along the $[1\bar{1}0]$ after the M band had been bleached partially with light polarized along the $[110]$ in this band.

in the F band or with the distortion of the crystalline field of the F centre through an anisotropic effect of the M centre. To determine experimentally which of these two possibilities is probable, a quantitative analysis of dichroism both in the F and M bands was carried out.

In Fig. 15 (a), the curve (1) shows absorption spectrum for the initial state of the specimen. After the M band was developed at 17°C by illuminating with light polarized along the $\langle 100 \rangle$ in the F band (the curve (2) in Fig. 15 (a)), the M band was bleached partially with light polarized along the $[1\bar{1}0]$ in its band ($\lambda=820\text{ m}\mu$, band pass=50 m μ). Variations of dichroism in the F and M bands with the period of illumination are shown in Fig. 16 (a), and the spectra at the illuminating period of 120 min are also shown in Fig. 15 (a). A spectral distribution of dichroism $D \equiv A_{[110]} - A_{[1\bar{1}0]}$ at this instant is plotted in Fig. 15 (b), in which the shaded region indicates the negative value of D . It is clearly observed that the peak of the M band measured with light polarized either along the $[110]$ or $[1\bar{1}0]$ shifted from 820 m μ to 825 m μ when it was illuminated with light polarized along the $[1\bar{1}0]$ in this band for 120 min (see, Fig. 15 (a)). The peak of dichroism in the M band region coincides with that of the M band, and the half width of its dichroism is also equal to that of the M absorption band.

Now, if dichroism in the F band is caused by the second band of the M centre, the ratio $|D_M/D_F|$ should remain a constant value during the course of partial bleaching of the M band, where D_M and D_F are dichroism at the peak of the M and F bands, respectively. This is shown in Fig. 16 (c). The mean value of the ratio was 2.02 ± 0.20 which is represented by a full line in the figure:

$$|(D_M/D_F)_{exp}| = 2.02 \pm 0.20. \quad (28)$$

Kanzaki⁹⁾ and Kawabara and Mitsu¹⁰⁾ measured recently the ratio and obtained the value of $1/0.50$ and $1/(0.50 \pm 0.05)$, respectively. They agrees quite well with the present value.

On the other hand, the ratio is calculated with use of Eq. (23), under the assumption that the absorption peak of the second M band coincides with that of the F band and that dichroism D_F is caused only by the second band of the M centre:

$$\begin{aligned} (D_M/D_F)_{calc} &= (H_{M2}/f_{M2}) \cdot (f_{M1}/H_{M1}) \\ &= \frac{1}{2(p-1)} \cdot \frac{H_F}{f_F \cdot H_{M1}} \end{aligned} \quad (29)$$

Especially at room temperature, the ratio has the next numerical value (cf. Eq. (23a)):

$$(D_M/D_F)_{calc} = 0.32 \cdot (0.83/0.13) \simeq 2.0,$$

or

$$1/(D_M/D_F)_{calc} \simeq 0.50, \text{ at room temperature.}$$

Hence, we have

$$|(D_M/D_F)_{exp}| \simeq (D_M/D_F)_{calc}. \quad (30)$$

Thus, it is certain that dichroism in the F band is mainly caused by dichroism in the second band of the M centre hidden in the F band.

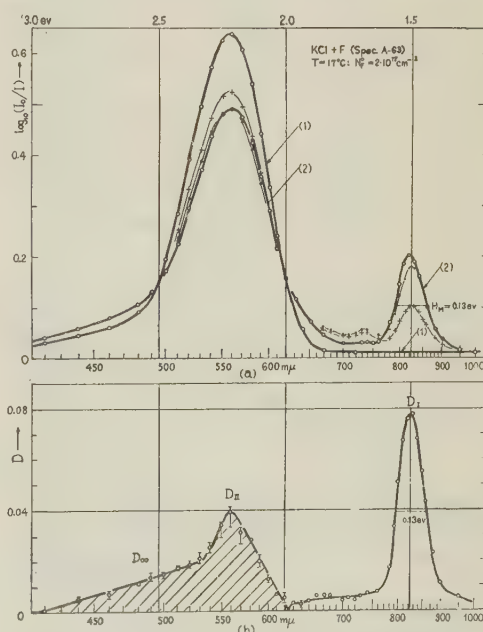


Fig. 15 (a) and (b). Dichroism in the F and M bands induced at 17°C by illuminating with light polarized along the $[1\bar{1}0]$ in the M band.

(a): Absorption spectra of the specimen. The curve (1) shows absorption spectrum for the initial state at 17°C, the curve (2) for the state after the M band was developed by illuminating with F band light polarized along the $\langle 100 \rangle$. The curve $-\cdot-\cdot-$ and $-+--+$ are the absorption spectra measured with light polarized along the $[110]$ and $[1\bar{1}0]$, respectively, after the M band (curve (2)) was bleached partially with $[1\bar{1}0]$ polarized M band light ($\lambda=820\text{ m}\mu$, band pass=50 m μ) for 120 min at 17°C.

(b): Spectral distribution of dichroism defined by $A \equiv D_{[110]} - A_{[1\bar{1}0]}$ (see, the text). Each point plotted in the figure is a mean value of repeated measurements.

Fig. 15 (b) shows, however, that dichroism in the F band appears in a wide spectral region extending into the short wavelength branch of the F band and it has a peak which located at $\sim 560\text{ m}\mu$. We term it D_{II} . It may be possible to conclude that D_{II} is responsible for the experimental evidence that the second M band exists in the spectral region of the F band, in view of argumentations and results in § 6 and Eq. (30). The half width of D_{II} varied from specimens to speci-

mens. However, it has certainly the value of about 0.20 eV which is far greater than the one evaluated in § 6, *i.e.*, 0.054 eV (Eq. (23b)). The discrepancy is hardly explicable with our data so long as it is assumed that the half width D_{II} is equal to that of the second M band as was the case for the first M band and D_I .

On the other hand, it is necessary to consider that dichroism in the short wavelength branch, D_∞ , is caused by the other origin. As stated in §§ 4 and 5, when the specimen exposed to F band light at room temperature was heated above 130°C , it contains certainly only F and M centres at first, and then the spectrum recovers to the initial state which exhibits only the F band, owing to the thermal dissociation of M centres into F centres. It should be emphasized here that the increment of absorption in the spectral region both of the K band and the short wavelength branch of the F band vanishes completely. Secondly, when the pure M band exists as shown in Fig. 9 (§ 5), the absorption is always enhanced in the above spectral region. For three specimens A-17, -18 and -20 of Table I, the ratio of the optical density at $820\text{ m}\mu$ to the increment at $460\text{ m}\mu$, $r_1 \equiv (\Delta A_{820}/\Delta A_{460})$, is considered to be constant (see, Table II-A). Finally, when the M centres were completely converted into F centres by irradiation with M band light at 125°C , in which case prior to light exposure the specimen contained naturally only F and M centres, the spectrum in the short wavelength branch of the F band recovered to its original state. These three facts indicate that the increment of the absorption in the short wavelength branch of the F band is directly related to the M centre, when the specimen contains only F and M centres. Especially, the last phenomenon rules out another possible interpretation that the above increment of the absorption is caused by another kind of colour centre which is quite independent of the M centre and dissociates thermally into F centres in the same temperature range as that of the M centre. Thus, it may be possible to interpret that the increment of absorption stated above corresponds to a continuous absorption of the M centre, and that dichroism in the shorter wavelength side of D_{II} is ascribed its origin to this. This interpretation is also supported by

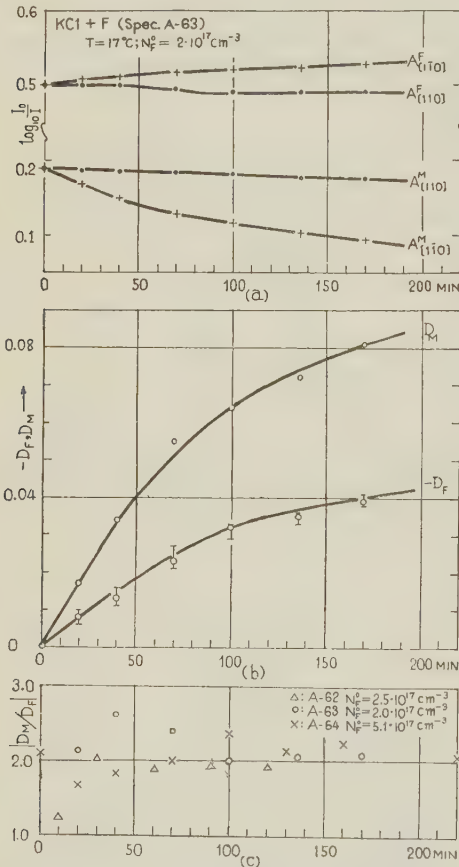


Fig. 16. Variation of dichroism in the F and M band with the period of illumination with M band light polarized along the $[1\bar{1}0]$. Each point in the figure is a mean value of repeated measurements. (a): Variation of the optical density at the peak of the F and M bands measured with light polarized along the $[110]$ and $[1\bar{1}0]$. Notations for the curve are the same as that of Fig. 15(a). (b): Variation of D_M and D_F with the period of illumination. (c): Experimental values of the ratio $|D_M/D_F|$ mean value is at every stage of illuminating period and their respresented by the full line.

the fact that the ratio $\Delta N_F / \Delta(f_M \cdot N_M)$, that was obtained in the circumstance that the increment of the absorption area in the short wave length branch of the F band amounted to a considerable part of the absorption area of the M main band (see, Fig. 9 (a)), is equal to the ratio η_F / η_M obtained above 130°C by another procedure.

In the photochemical reaction with F band light at room temperature, however, we observe the phenomenon which appears to be contradicted to the above interpretation at first sight: The absorption in the short wave length branch of the F band increase continuously even when the M band is lowered at a later stage of the photochemical reaction. One sees this at once by comparison of the curve II with 3 in Fig. 2 (b). Table II-B contains values of the increment of the optical density at $\lambda = 820 \text{ m}\mu$ and $460 \text{ m}\mu$, ΔA_{820} and ΔA_{460} , and the ratio $r_2 = (\Delta A_{820} / \Delta A_{460})$ at every stage of illumination with F band light ($\lambda = 555 \text{ m}\mu$, band pass = $20 \text{ m}\mu$) at 12°C. The illumination period of the table covers the stage including the linearly ascending part and the descending part beyond the maximum plateau of the developing curve of the M band. In this stage, the absorption maximum of the R_2 band rises linearly, as shown in Fig. 2 (a). Now, the ratio r_1 of the specimen containing only F and M centres has a mean value of 13, while the corresponding ratio r_2 for the specimen illuminated with F band light amounts to about 60% of the former, at the stage of the linear part of the M-curve (Table II-A & B). According to the analysis of § 8, ~70% of the electrons of the photochemically destructed F centres is used to create M centres and the remainder is consumed for the construction of the other complex centres, in this stage. Therefore, it is certain that the increment of the optical density in the short wavelength branch of the F band is caused both by the continuous absorption of the M centre on the one hand and by that of the other complex centres (presumably mainly of the R centre, at the present experiment) on the other hand, when the F band was irradiated with light in the F band at room temperature. Then, the fact that the optical density in the above spectral region continues to increase even when the M band is lowered is not contradicted to the inter-

Table II.

A: ΔA_{820} , ΔA_{460} and the ratio $r_1 = (\Delta A_{820} / \Delta A_{460})$ for the specimen containing only F and M centres.

Specimen	ΔA_{820}	ΔA_{460}	r_1
A-17	0.331	0.034	~10
A-18	0.152	0.010	~15
A-20	0.064	0.005	~13

Mean Value ≈ 13

B: ΔA_{820} , ΔA_{460} and the ratio $r_2 = (\Delta A_{820} / \Delta A_{460})$ at every stage of illumination with F band light at 12°C. $N^\circ_F = 3 \cdot 10^{17} \text{ cm}^{-3}$.

Period of Illu. (Min)	ΔA_{820}	ΔA_{460}	r_2
15	0.101	0.015	6.7
25	0.198	0.027	7.3
35	0.291	0.038	7.7
55	0.423	0.058	7.3
75	0.468	0.077	6.1
95	0.453	0.085	5.3

pretation stated above. In facts, the absorption in the above branch is lowered when the M band is illuminated with light in this band at room temperature.

Thus, the evidences and considerations given here permit us to conclude the followings:—

- (i) The second band of the M centre exists in the F band, and dichroism D_{II} is conceived to be responsible for the experimental evidence.
- (ii) The M centre has further the other absorption in the shorter wavelength region in the F band. This is detected as the increment of the absorption in the short wavelength branch of the F band. Dichroism in the above branch, D_∞ , is conceived to be due to this absorption.
- (iii) When the F band is illuminated with light in this band at room temperature, the absorption of its short wavelength branch is enhanced. One part of the increment is due to the M centre, and the other part mainly to the absorption other than the main band of the R (or R and N) centre.

§ 8. The Anomaly on the Bleaching Curve of the F band

In the preceding section, it was concluded

that the second M band exists in the spectral region of the F band. It is anticipated from the above conclusion that the bleaching curve of the F band might exhibit some dependency on the wavelength of light with which it was irradiated. To carry out this experiment, the F band was illuminated with monochromatic light of 620, 605, 585, 575, 560, 545, 530 and 510 m μ . The band pass was chosen 8 m μ for each "probe" light except the first and the last whose band pass was 10 m μ . The experiment was made both on the freshly coloured crystal and on the crystal left in the dark for two months after colouration. The obtained results showed a fairly good agreement irrespective of the aging period of the specimen.

In Fig. 17 (a) and (b), the bleaching curves for the F band were shown for light lying in the longer wavelength side in the spectral region of the F band and for those in the shorter, respectively. The optical density was measured at 560 m μ throughout this experiment. In connexion with this, the developing curves for the A, R, M and N bands were shown in Fig. 17 (c) only for the specimen which was illuminated with light of 560 m μ (curve (4)), for simplicity. The part *pq* of the bleaching curve mainly corresponds to the F to A transformation at the beginning. In fact, as shown by the curve (1) in Fig. 17(a), the inclination of the *pq* is affected when the F band was illuminated with light 620 m μ which lies also in the A band. Near the end of the stage *pq*, the A-curve reaches its maximum height, and, at the same time, the linear increase of the M-curve is already initiated. At this instant, the anomaly *qr* appears on the bleaching curve and was inferred by St. Petroff as the B state. The subsequent part *rs* is considered to correspond mainly to the F to (M+R)-transformation. In fact, the ratio of the inclination *rs* to that of the M-curve was independent of the wavelength of illuminating light and gave a mean value $|0.98| \pm 0.09$. Since, according to Eq. (10), it is calculated that the ratio should be $|0.66|$ if the F to M transformation takes place, 30% of electrons of the destructed F centres is used to create the other complex centres but M centres even at the beginning of the stage *rs*. It is clearly seen from Fig. 17 (a) that the duration of the stage *qr*

becomes longer and that of the *rs* shorter, as the wavelength of illuminating light is shorter. Really, *rs* vanishes on the curve (4), in which the wavelength of illuminating light was 560 m μ , and any anomaly cannot be seen. The ratio of the inclination *qr* to that of the M-curve has a mean value $|0.70|$. Accordingly, in the stage *qr*, almost all of the electrons of the destructed F centres was used to create M centres and the ratio of the inclination of *st* to that of the R-curve was, consequently, suppressed to a lower value ($\approx |0.6|$) for the specimen having a longer period of *qr*, while for the specimens having not any or a shorter period of *qr*, the ratio was raised to $|1.6| \sim |1.2|$.

The situation is altered in the ultra violet side in the F band. The curve (1)' of Fig. 17 (b) does not carry any anomaly and is quite

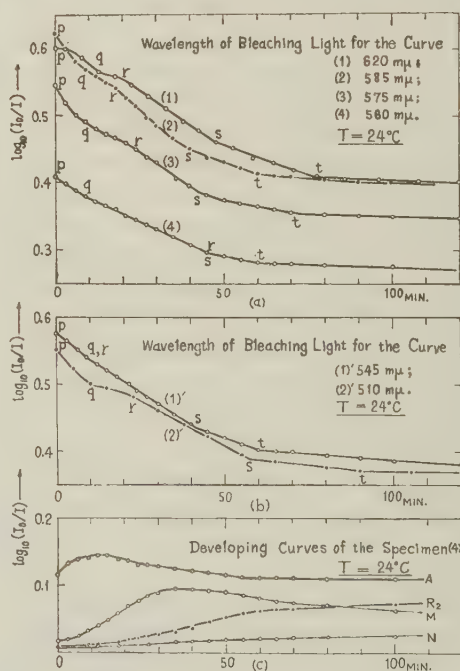


Fig. 17. Dependency of the bleaching curve of the F band on the wavelength of light with which it was illuminated. The absorption was measured at 560 m μ .

(a): The bleaching curves of the F band which was illuminated with light 620, 585, 575 and 560 m μ at 24°C (the curve (1), (2), (3) and (4), respectively).

(b): The bleaching curve of the F band irradiated with light 545 and 510 m μ at 24°C .

(c): The developing curves for the complex centres in the specimen shown by the curve (4) in (b).

similar to the curve (4) in the shape. However, the stage subsequent to the pq should not be assigned to qr , but to rs , because the ratio of the inclination of this part to that of the M-curve is equal to $|1.0|$. This type of the bleaching curve was obtained also on the specimen irradiated with light of $530\text{ m}\mu$. On the curve (2)', in which the specimen was irradiated with light of $510\text{ m}\mu$, the anomaly qr reappears. As shown in Fig. 2 (a), the anomaly was detected on the bleaching curve for the F band. Since the specimen was illuminated with light of $545\text{ m}\mu$ whose band pass is $20\text{ m}\mu$, it is conceived that the F-curve in Fig. 2 (a) represents the combined feature both of curve (4) and (1)' in Fig. 17.

According to the result that 30% of the electrons of the destructed F centres is used to create R and N centres even at the earlier stage where the M-curve initiated its linear rise, it is certain that the photochemical reaction with F band light is essentially characterized by the simultaneous production of M, R and N centres, at room temperature. It has also shown in § 6 (Fig. 13) that nearly equal fraction of the electrons of the destructed M centres is consumed in the construction of the R and N centres.

The dependency of the rate of the photochemical reaction on the wavelength of light with which it was carried out may indicate the complexities hidden under the F band. For the definite assignment of the stage qr to the B centre or to the second M band through which some special interaction between F and M centres might be elucidated, however, further experiments will be required.

§ 9. Discussions

9.1. The M centre

On the basis of experiments on dichroism in the M band induced by illumination with light polarized along the $\langle 110 \rangle$ in this band, it has been concluded that the optical dipolemoment of the M centre is directed to the special crystallographic direction except the $\langle 100 \rangle$ and this centre has not a cubic symmetry. It is easily calculated that one third of the total number of the M centre is detected by an optical absorption measurement either with *natural* or with *plane polarized* light when its dipolemoment is directed to

the $\langle h, k, l \rangle$ direction as shown in Table III, in which (i) $h \neq k \neq l$ and $h \neq 0, k \neq 0, l \neq 0$; (ii) $h \neq k \neq l$ and $h \neq 0, k \neq 0, l = 0$; (iii) $h = k \neq l$ and $h \neq 0, k \neq 0, l = 0$; (iv) $h = k \neq l$ and $h \neq 0, k \neq 0, l = 0$ and (v) $h = k = l \neq 0$.

In our experiment, the relation (14b), $\eta_F = 0.56$, was interpreted that the M centre carries one electron. However, the relation (10), which determined the ratio of the number of F centres corresponding to one M centre, does not specify any definite model for the M centre, but only put the restriction $f_M < 1$ in order not to be contradicted to Eq. (14b). Since the relation (17), (18), (19) and (20) are influenced only by the parameter p , the overlapping factor of the second M band with the F band, they are equally valid for any kind of the M centre whose optical dipolemoment is parallel to the arbitrary $\langle h, k, l \rangle$ crystallographic direction.

If it is possible to assign to the M centre the model whose optical dipolemoment is parallel to the crystallographic direction having a lower index, the $\langle 110 \rangle$ or the $\langle 111 \rangle$, the $\langle 110 \rangle$ -M centre is preferable according to the Ishii's analysis²⁶⁾: Under the assumption that the M centre is either the $\langle 110 \rangle$ - or $\langle 111 \rangle$ -type, it was concluded for the thermal reorientation of the M centre in the direction that the dichroism $D \equiv A_{[110]}^M - A_{[1\bar{1}0]}^M$ vanishes, where $A_{[110]}^M > A_{[1\bar{1}0]}^M$ at the time $t = 0$, as follows: (i) The reorientation of the optical dipolemoment takes place with equal frequency $1/\tau$ for six possible directions, (ii) $-dA_{[110]}^M = dA_{[110]}^M$ for the $\langle 111 \rangle$ -M centre and (iii) $-dA_{[110]}^M > dA_{[1\bar{1}0]}^M$ for the $\langle 110 \rangle$ -M centre and this relation agrees quite well with the experimental fact¹¹⁾.

If the M centre carries two electrons, the quantum yield of the F centre η_F may be too small, because all the electrons ejected from M centres should be captured either by Cl^- vacancy or by the M-vacancy owing to the relation $\eta_F = -2\eta_M$. In fact, if it is postulated that the second band of the M centre of two-electron system exists in the spectral region of the F band so as to make the net quantum yield a quantum equivalent full value, i.e., $\eta_F^* = 2.0$, then the next relation should be valid [cf. Eqs. (10), (22)]:

$$\Delta K_{M2}/\Delta K_{M1} = D_{M2}/D_{M1} = 1.6.$$

at room temperature.

Then, we have to admit, in this case, some

effect of the F band which suppresses dichroism in this band down to the observed value of 0.50. Therefore, it is conceived that such a model of the M centre as proposed by van Doorn will be discarded. Thus the descriptions of §§5–8, which based on the one-electron model of the M centre, are justified.

Now, it is possible to state, in conclusion, that the concentration of the M centre per

cm³ N_M^* is calculated, without specifying its model, by the next equation:

$$N_M^* = 1.06 \cdot 10^{16} \frac{3}{f_{M1}} \cdot K_M \cdot H_M \\ = 3.83 \cdot 10^{16} \cdot K_M \cdot H_M \tag{31}$$

where K_M in cm⁻¹ is the maximum absorption coefficient of the M band determined by absorption measurement, and H_M in eV is the half width of this band.

Table III. The ratio of the number of the optically detected dipolemoment to that of those directing to the $\langle k, h, l \rangle$ crystallographic direction.

Index	The number of possible independent orientation of dipolemoment	The number of dipolemoment detected optically	Ratio
$\langle h, k, l \rangle \ h \neq k \neq l \neq 0$	24	8	1/3
$\langle h, k, l \rangle \ h \neq k \neq l, \ l = 0$	12	4	1/3
$\langle h, k, l \rangle \ h = k \neq l = 0$	12	4	1/3
$\langle 1, 1, 0 \rangle \ h = k, \ l = 0$	6	2	1/3
$\langle 1, 1, 1 \rangle$ (Forbidden) $h = k = l \neq 0$	4	4/3	1/3
$\langle 1, 0, 0 \rangle$ (Forbidden) $h \neq 0$ $k = l = 0$	3	1	1/3

9.2. Dichroism

According to the conclusion drawn in §7–(ii), it is certain that the second and the other absorption including the continuous one of the M centre exist in the spectral region of the F band and of its short wavelength side. In addition to this, if the conclusion §7–(iii) is taken into considerations, it may not be quite unreasonable to infer that the R centre has also its absorption band hidden under the main band of the F centre. Then, the phenomenon that the R and M bands become dichroic when the F band was made dichroic by illuminating with light polarized along the $\langle 110 \rangle$ in this band is easily recognized. On the other hand, the F band becomes dichroic when the R band was made dichroic by illumination with polarized light in this band. It is conceived that the absorption band of the R centre hidden under the F band plays its role in producing dichroism in the F band, in a quite similar way to the M band (§7). It is, however, observed that R, M and F bands become dichroic simultaneously when the R or M band was made dichroic by illuminating with polarized light in the R or M band, respectively. To explain this phenomenon completely, we have to admit the intimate interaction between the

R and M centres (presumably including F centres) which is unknown at present.

9.3. Some aspect of photochemical reactions at room temperature

It is generally observed that, among the developing curves of complex centres, only the M-curve descends at a later stage of the photochemical reaction carried out at room temperature by illumination with F band light. However, when the F band is illuminated with light polarized along the $[110]$ in this band, the corresponding phenomenon is observed only on the M-curve measured with light polarized along the direction normal to the polarization direction of F band light with which the F band was illuminated, as shown by the $A_{[110]}^M$ -curve of Fig. 14 (a). If the M band is lowered by a process whereby the M centre captures another electron to transform into the R_2 centre, the above phenomenon should be observed equally on the $A_{[110]}^M$ -curve of Fig. 14 (a). Therefore, it appears to be plausible that the special behaviour of the M-curve is caused by the destruction of M centres through absorption of F band light by the second M band hidden in the F band: Suppose that the specimen contains N_M M centres per cm³ at a given time t and that

incident light $I_{0,F}$ of the F band region falls upon it, then the destructed M centres dN_M in a time interval dt may be expressed by

$$dN_M = k \cdot I_{0,F} \cdot N_M \cdot dt,$$

where k is a constant; if a fraction γ of the dN_M electrons is consumed in the construction of the R_2 centre, its increment dN_{R_2} per dt should be described by

$$dN_{R_2}/dt \propto K \cdot N_M,$$

$$K = \frac{1}{\gamma} k I_{0,F} = \text{const.} \quad (32)$$

This is nothing else the experimental law obtained by St. Petroff²⁾. Of course, it is not clear at present that the R_2 centre is created only by the process stated above when the F band was illuminated with light in the F band at room temperature.

§ 10. Summaries

1. The photochemical reaction with F band light was reexamined for KCl crystal coloured additively. In a temperature range from -70°C to 165°C , it was classified into three types: The photochemical reaction which creates (i) the A, R_1 , R_2 , M and N centres (-50°C to 50°C), (ii) the A, R_3 , M and N centres (60°C to 100°C) and (iii) the M and the higher aggregates of F centres presumably (at 165°C), as photochemical products (§ 3).

2. The above phenomena were considered to be due to the thermal stability of these products and their thermal stability was studied (§ 4). The R_1 and R_2 centres were unstable thermally above 50°C and they decomposed into the R_3 , N, M and F centres. By this thermochemical reaction, the N band was enhanced to the height which was hardly attainable by illumination with F band light at room temperature. R_3 and N centres dissociated into F and M centres above 100°C . M centres were thermally the most stable and dissociated into F centres above 130°C . The relaxation time for the process is expressed as $1/\tau = 2.01 \cdot 10^{12} \exp(-1.31/kT) \text{ sec}^{-1}$ for kT in eV.

3. The fact, that the M centre is thermally the most stable among the photochemical products, enabled us to determine the number of F centres corresponded to one M centre. The relation $\Delta N_F / \Delta(f_M N_M) = -2$ was obtained (§ 5).

4. The quantum yield $\eta_F \equiv \partial N_F / \partial q_M$ and

$\eta_M \equiv \partial(f_M N_M) / \partial q_M$ were determined in the reaction $M + q_M \rightarrow F$ as a function of temperature (§ 6). The relations $\eta_F = 0.56$ and $\eta_F = -2\eta_M$ were obtained above 130°C where M centres decompose thermally into F centres. Thus, it was concluded that the M centre carries one electron and has the second band in the spectral region of the F band with an overlapping factor $p = 1.8$. The oscillator strength of the main band of the M centre was 0.83, and the ratio of the half width to the oscillator strength of the second M band was 0.32 at room temperature. The net quantum yield of the M centre η_M^* was expressed as $1/\eta_M^* = 1 + 1.4 \cdot 10^{-7} \exp(0.50/kT)$ for kT in eV.

5. Dichroism of the F band induced by illumination with light polarized along the $\langle 110 \rangle$ in the M band was analysed quantitatively (§ 7), with use of the value of overlapping factor p . This led to the conclusion that dichroism of the F band is ascribed to that of the second and the other absorption of the M centre.

6. It is concluded that the increment of the absorption in the short wavelength branch of the F band is due to the other absorption both of the M and R centres, when the F band was illuminated with light in this band at room temperature (§ 7).

7. The anomaly on the bleaching curve of the F band measured at $560 \text{ m}\mu$ was re-examined (§ 8). It was found that it appears showing strong dependency of the wavelength of light with which the F band was illuminated.

It is a great pleasure for the author to express his cordial thanks to Prof. M. Ueta for his kind interest and encouragement, and to Profs. F. Seitz and R. Maurer for their kind interest.

References

- 1) R. Ottmer: Z. Phys. **46** (1928) 798.
- 2) St. Petroff: Z. Phys. **127** (1950) 443.
- 3) N. Barth: Z. Phys. **149** (1957) 370.
- 4) F. Seitz: Rev. Mod. Phys. **18** (1946) 384; *ibid.* **26** (1954) 7.
- 5) R. S. Knox: Phys. Rev. (L) **2** (1959) 87.
- 6) A. W. Overhauser and H. Rüdhardt: Phys. Rev. **112** (1958) 722.
- 7) M. Ueta: J. Phys. Soc. Japan **7** (1952) 107.
- 8) J. Lambe and W. D. Compton: Phys. Rev.

- 106** (1957) 684.
- 9) H. Kanzaki: Phys. Rev. **110** (1958) 1063.
 - 10) G. Kuwabara and A. Misu: J. Phys. Soc. Japan **13** (1958) 1038.
 - 11) T. Ishii, T. Tomiki and M. Ueta: J. Phys. Soc. Japan **14** (1959) 1415.
 - 12) C. Z. van Doorn: Philips Res. Rept. **12** (1957) 309.
 - 13) H. Okura: J. Phys. Soc. Japan **12** (1957) 1313.
 - 14) K. H. Becker and H. Pick: Nachr. Akad. Wiss. Göttingen (**1956**) 167.
 - 15) A. B. Scott and L. P. Bupp: Phys. Rev. **79** (1950) 341.
 - 16) A. B. Scott, L. P. Bupp and M. Thompson: J. Phys. Chem. **57** (1953) 757.
 - 17) A. B. Scott, and G. W. Neilson: *Defects in Crystalline Solids*, Report of Bristol Conference (Phys. Soc. London, 1955) 297.
 - 18) H. Pick: Ann. Physik (5) **31** (1938) 365.
 - 19) T. Tomiki: J. Phys. Soc. Japan **14** (1959) 1114.
 - 20) F. G. Kleinschrod: Ann. Physik (5) **27** (1936) 97.
 - 21) A. Smakula: Z. Phys. **59** (1930) 603.
 - 22) T. Tomiki: J. Phys. Soc. Japan **14** (1959) 1248.
 - 23) E. Mollwo: Z. Phys. **85** (1933) 56.
 - 24) N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals*, (Oxford, 2nd ed. Clarendon Press, 1946) chap. 4.
 - 25) T. Ishii: Sci. Repts. Tohoku Univ. (Series 1, **XLIII** (1959) 67.
 - 26) F. Lütty: Z. Phys. **145** (1956) 249.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 3, MARCH, 1960

On the Acoustic Radiation from a Flanged Circular Pipe

By Yûkichi NOMURA, Ichirô YAMAMURA and Sakari INAWASHIRO

Department of Applied Science, Tôhoku University

(Received July 4, 1959)

The problem of sound radiation from a circular pipe fitted with an infinite flange is solved. The radiation impedance, the transmission coefficient, the power gain function and the end correction are evaluated numerically and shown as functions of the wave length.

§1. Introduction

The problem of sound radiation from an unflanged circular pipe was solved by H. Levine and J. Schwinger in 1947.¹⁾ Using a Green's function, they formulated the problem in terms of an integral equation similar to the equation of Wiener-Hopf type and solved it by application of the Fourier transform method. In case of a flanged circular pipe, a Green's function consists of two terms, one representing free space propagation of sound, with dependence on $z-z'$, and the other representing the image effect of the flange, with dependence on $z+z'$. As they remarked in their paper, the existence of the latter term considerably complicates the Fourier transform solution.²⁾

We will solve this problem by the use of Weber-Schafheitlin type integrals³⁾ and Jacobi's polynomials.⁴⁾ We consider the two

space regions, the one outside the flanged pipe and the other within the pipe. The two solutions that satisfy the wave equation and the boundary conditions in each region are obtained and connected smoothly at the open end of the flanged pipe. The continuity conditions for the wave function itself and for its derivative in the direction of the pipe axis give two equations, from which we can determine unknown coefficients in the solution.

§2. Solution of the Problem

We consider the sound radiation from the pipe which is fitted with an infinite flange. A cylindrical coordinate system is chosen with origin at the center of the pipe mouth, and oriented so that the flange lies in the x, y plane. A plane wave is incident from the negative z direction and a part of its energy is radiated from the open end into the

free half space $z > 0$, and the remainder is reflected back into the pipe.

The velocity potential of the incident wave is described by a scalar wave function

$$\phi_0 = \frac{V_0}{k} \exp\left(\frac{-i\gamma z}{a}\right), \quad (2.1)$$

where $\gamma = ka$ is a parameter depending on the wave number k and the pipe radius a , and V_0 the velocity amplitude of the incident wave. The harmonic time dependence $e^{i\omega t}$ (ω is the frequency of the wave) is omitted throughout. We put

$$\phi_1 = \frac{V_0}{k} \left\{ a_0 \exp\left(\frac{i\gamma z}{a}\right) + \sum_{s=1}^{\infty} a_s J_0\left(\beta_s \frac{r}{a}\right) \exp\left(\sqrt{\beta_s^2 - \gamma^2} \frac{z}{a}\right) \right\}, \quad (2.2)$$

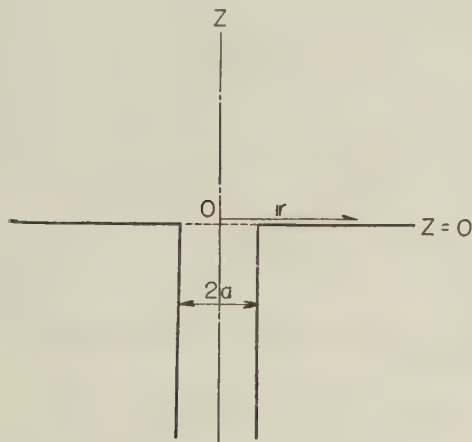


Fig. 1.

as an expression for the reflected wave within the pipe, where β_s are positive zeros of $J_0'(\beta_s) = -J_1(\beta_s) = 0$, and

$$\phi_2 = \frac{V_0}{k} \sum_{n=0}^{\infty} A_n S_n\left(\frac{r}{a}, z\right), \quad (z > 0) \quad (2.3)$$

for the radiated wave outside the pipe, where

$$S_n\left(\frac{r}{a}, z\right) = \int_0^{\infty} \frac{\sqrt{\xi} J_0\left(\frac{r\xi}{a}\right) J_{2n+\frac{1}{2}}(\xi) \exp\left(-\sqrt{\xi^2 - \gamma^2} \frac{z}{a}\right)}{\sqrt{\xi^2 - \gamma^2}} d\xi, \quad z > 0. \quad (2.4)$$

Conditions upon the velocity potential are given as follows;

$$\frac{\partial}{\partial r}(\phi_0 + \phi_1) = 0 \quad r = a, \quad z < 0, \quad (2.5)$$

$$\frac{\partial}{\partial z} \phi_2 = 0 \quad r > a, \quad z = 0, \quad (2.6)$$

$$\phi_0 + \phi_1 = \phi_2 \quad r < a, \quad z = 0, \quad (2.7)$$

$$\frac{\partial}{\partial z}(\phi_0 + \phi_1) = \frac{\partial}{\partial z} \phi_2 \quad r < a, \quad z = 0. \quad (2.8)$$

In the half space $z > 0$, the field at distant points from the open end of the pipe should be asymptotically described by a divergent travelling wave, i.e.

$$\phi_2 \sim \frac{1}{R} \exp\left(\frac{-i\gamma R}{a}\right), \quad (R = \sqrt{r^2 + z^2}) \quad (2.9)$$

where we suppressed dependence on direction.

From the forms of (2.1) and (2.2), it is easily seen that $\phi_0 + \phi_1$ satisfies (2.5), with vanishing normal derivative on the surface of the pipe wall. The radiation field ϕ_2 in (2.3) satisfies (2.6), on account of a property of the function S_n

$$\begin{aligned} \frac{\partial}{\partial z} S_n\left(\frac{r}{a}, 0\right) &= -\frac{1}{a} \int_0^{\infty} \sqrt{\xi} J_0\left(\frac{r\xi}{a}\right) J_{2n+\frac{1}{2}}(\xi) d\xi \\ &= 0 \quad \left(\frac{r}{a} > 1\right), \end{aligned}$$

where the integral is a type of Weber-Schafheitlin integrals.³⁾ The asymptotic behavior (2.9) is ensured by the values of S_n for large R which is obtained by the saddle point method.⁵⁾ The remaining conditions (2.7) and (2.8) which connect $\phi_0 + \phi_1$ and ϕ_2 are written in terms of the expansion coefficients A_n and a_s as follows,

$$\sum_{n=0}^{\infty} A_n S_n\left(\frac{r}{a}, 0\right) = 1 + a_0 + \sum_{s=1}^{\infty} a_s J_0\left(\beta_s \frac{r}{a}\right), \quad (2.10)$$

$$\begin{aligned} \sum_{n=0}^{\infty} A_n a \frac{\partial}{\partial z} S_n\left(\frac{r}{a}, 0\right) &= i\gamma(a-1) + \sum_{s=0}^{\infty} a_s \sqrt{\beta_s^2 - \gamma^2} J_0\left(\beta_s \frac{r}{a}\right). \quad (2.11) \end{aligned}$$

From these two equations, we can determine the unknown coefficients A_n and a_s .

§3. Determination of the Coefficients

Using the expansion formula⁶⁾

$$f(x) = \sum_{n=0}^{\infty} c_n u_n(x) \quad (0 < x < 1)$$

$$c_n = \frac{4n+1}{\sqrt{2}\Gamma(n+\frac{1}{2})} \int_0^1 f(x) \frac{d^n}{dx^n} \{x^n(1-x)^{n-\frac{1}{2}}\} dx,$$

where $u_n(x)$ is a Jacobi's polynomial

$$u_n(x) = \frac{\Gamma(n+\frac{1}{2})}{\sqrt{2}(n!)^2} (1-x)^{\frac{1}{2}} \frac{d^n}{dx^n} \{x^n(1-x)^{n-\frac{1}{2}}\}, \quad (0 < x < 1)$$

we obtain

$$S_n(\sqrt{x}, 0) = \sum_{l=0}^{\infty} G_{nl} u_l(x) \quad \left(x = \left(\frac{r}{a}\right)^2\right) \quad (3.1)$$

$$G_{nl} = (4l+1) \int_0^{\infty} \frac{J_{2n+\frac{1}{2}}(\xi) J_{2l+\frac{1}{2}}(\xi)}{\sqrt{\xi^2 - \gamma^2}} d\xi, \quad (3.2)$$

and

$$J_0(\beta_s \sqrt{x}) = \sum_{l=0}^{\infty} (4l+1) \frac{J_{2l+\frac{1}{2}}(\beta_s)}{\sqrt{\beta_s}} u_l(x). \quad (3.3)$$

Substituting (3.1) and (3.3) in (2.10), we have a set of equations relating A_n to a_s .

$$\begin{aligned} \sum_{n=0}^{\infty} A_n G_{nl} &= (1+a_0) \sqrt{\frac{2}{\pi}} \delta_{l0} \\ &+ (4l+1) \sum_{s=1}^{\infty} a_s \frac{1}{\sqrt{\beta_s}} J_{2l+\frac{1}{2}}(\beta_s), \quad (3.4) \\ (l=0, 1, 2, \dots). \end{aligned}$$

On the other hand, (2.11) is expanded in terms of Bessel functions $J_0(\beta_s r/a)$.

$$\begin{aligned} \sum_{n=0}^{\infty} A_n \left\{ T_{n0} + \sum_{s=1}^{\infty} T_{ns} J_0\left(\frac{\beta_s r}{a}\right) \right\} \\ = i\gamma(a_0 - 1) + \sum_{s=1}^{\infty} a_s \sqrt{\beta_s^2 - \gamma^2} J_0\left(\frac{\beta_s r}{a}\right), \quad (3.5) \end{aligned}$$

where T_{n0} and T_{ns} are given by

$$\begin{aligned} T_{n0} &= \int_0^1 a \frac{\partial}{\partial z} S_n(\rho, 0) d\rho \\ &= -2 \sqrt{\frac{2}{\pi}} \delta_{n0} \quad (3.6a) \end{aligned}$$

$$\begin{aligned} T_{ns} &= \frac{2}{[J_0(\beta_s)]^2} \int_0^1 a \frac{\partial}{\partial z} S_n(\rho, 0) J_0(\beta_s \rho) \rho d\rho \\ &= -\frac{2}{\sqrt{\beta_s} [J_0(\beta_s)]^2} J_{2n+\frac{1}{2}}(\beta_s). \quad (3.6b) \end{aligned}$$

From (3.5), we obtain the other set of equations

$$i\gamma(a_0 - 1) = -2 \sqrt{\frac{2}{\pi}} A_0 \quad (3.7a)$$

$$\begin{aligned} a_s \sqrt{\beta_s^2 - \gamma^2} &= -\frac{2}{\sqrt{\beta_s} [J_0(\beta_s)]^2} \sum_{n=0}^{\infty} A_n J_{2n+\frac{1}{2}}(\beta_s) \\ (s=1, 2, \dots) \quad (3.7b) \end{aligned}$$

giving expressions of a_s in terms of A_n .

From (3.4) and (3.7), we have a set of linear equations for A_n ,

$$\begin{aligned} \sum_{n=0}^{\infty} A_n G_{nl} &= 2 \left\{ 1 - \frac{1}{i\gamma} \sqrt{\frac{2}{\pi}} A_0 \right\} \sqrt{\frac{2}{\pi}} \delta_{l0} \\ &- (4l+1) \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{2 J_{2l+\frac{1}{2}}(\beta_s) J_{2n+\frac{1}{2}}(\beta_s)}{\beta_s \sqrt{\beta_s^2 - \gamma^2} [J_0(\beta_s)]^2} A_n. \quad (3.8) \end{aligned}$$

A matrix X_{ns} , an inverse of the matrix G_{nl} ,⁷⁾ is defined by

$$\sum_{n=0}^{\infty} G_{nl} X_{ns} = \delta_{ls} \quad (3.9)$$

and already calculated in the reference 7). Making use of the matrix X_{ns} , (3.8) is transformed into

$$A_n = 2 \left(1 - \frac{1}{i\gamma} \sqrt{\frac{2}{\pi}} A_0 \right) \sqrt{\frac{2}{\pi}} X_{n0} - \sum_{m=0}^{\infty} P_{nm} A_m \quad (3.10)$$

where

$$P_{nm} = \sum_{l=0}^{\infty} \sum_{s=1}^{\infty} (4l+1) X_{nl} \frac{2 J_{l+\frac{1}{2}}(\beta_s) J_{2m+\frac{1}{2}}(\beta_s)}{\beta_s \sqrt{\beta_s^2 - \gamma^2} [J_0(\beta_s)]^2}. \quad (3.11)$$

For the range of the values of γ under consideration ($\gamma < \beta_1 = 3.8317$), numerical calculation shows that X_{nm} and P_{nm} are quantities of the magnitude of order 1, for $n=m$, and decrease with a considerable rate as the difference $n \sim m$ increases. In order to obtain an approximate solution, we assume that A_n becomes smaller as n increases. (This assumption will be verified later). Then, the terms $P_{nm} A_m$ in the right hand side of (3.10), with $m > n$, are considerably small compared to the other terms, and if we neglect them, we obtain the following equations in the first approximation

$$A_n^{(0)} = 2 \left(1 - \frac{1}{i\gamma} \sqrt{\frac{2}{\pi}} A_0^{(0)} \right) \sqrt{\frac{2}{\pi}} X_{n0} - \sum_{m=0}^n P_{nm} A_m^{(0)}. \quad (3.12)$$

The equation for the deviation from the true solution is

$$\begin{aligned} (A_n - A_n^{(0)}) &= i \frac{4}{\pi \gamma} (A_0 - A_0^{(0)}) X_{n0} \\ &- \sum_{m=0}^n P_{nm} (A_m - A_m^{(0)}) - \sum_{m>n}^{\infty} P_{nm} A_m. \end{aligned}$$

If we take into consideration the effect of the last terms, $\sum_{m>n}^{\infty} P_{nm} A_m$, by replacing them by the approximate value of the largest term of them, i.e. by $P_{n, n+1} A_{n+1}^{(0)}$, we have

$$\left. \begin{aligned} A_n &\simeq A_n^{(0)} + A_n^{(1)} \\ A_n^{(1)} &= i \frac{4}{\pi} A_n^{(1)} X_{n0} - \sum_{m=0}^n P_{nm} A_m^{(1)} - P_{n, n+1} A_{n+1}^{(0)} \end{aligned} \right\} \quad (3.13)$$

in the second approximation. In the similar way, the $(q+1)$ -th approximation is given by

$$\left. \begin{aligned} A_n &\simeq A_n^{(0)} + A_n^{(1)} + \dots + A_n^{(q)} \quad q \geq 1 \\ A_n^{(q)} &= i \frac{4}{\pi} A_n^{(q)} X_{n0} - \sum_{m=0}^n P_{nm} A_m^{(q)} \\ &\quad - \sum_{m=1}^q P_{n, n+m} A_{n+m}^{(q-m)} \end{aligned} \right\} \quad (3.14)$$

Table I. Expansion coefficients A_n and a_0 .

γ	0.25	0.50	1.00	1.50	2.00	2.50	3.00	3.50
A_0	0.057	0.171	0.323	0.352	0.321	0.269	0.220	0.183
	$+i$ 0.292	$+i$ 0.501	$+i$ 0.748	$+i$ 0.961	$+i$ 1.208	$+i$ 1.498	$+i$ 1.817	$+i$ 2.165
A_1	0.019	0.054	0.061	- 0.016	- 0.137	- 0.258	- 0.335	- 0.303
	$+i$ 0.102	$+i$ 0.171	$+i$ 0.246	$+i$ 0.336	$+i$ 0.487	$+i$ 0.712	$+i$ 1.003	$+i$ 1.334
A_2	- 0.006	- 0.018	- 0.040	- 0.054	- 0.067	- 0.078	- 0.076	- 0.040
	$-i$ 0.031	$+i$ 0.039	$-i$ 0.081	$-i$ 0.101	$-i$ 0.116	$-i$ 0.121	$-i$ 0.107	$-i$ 0.078
A_3	0.003	0.011	0.024	0.034	0.043	0.051	0.058	0.061
	$+i$ 0.017	$+i$ 0.031	$+i$ 0.045	$-i$ 0.056	$+i$ 0.065	$+i$ 0.072	$+i$ 0.075	$+i$ 0.071
a_0	- 0.868	- 0.600	- 0.194	- 0.023	0.036	0.043	0.033	0.013
	$+i$ 0.365	$+i$ 0.546	$+i$ 0.516	$+i$ 0.374	$-i$ 0.256	$+i$ 0.172	$+i$ 0.117	$+i$ 0.083

The solutions of (3.12) and (3.14) are easily obtained and given by

$$\left. \begin{aligned} A_0^{(0)} &= i\gamma \sqrt{\frac{\pi}{2}} \frac{X_{00}}{X_{00} + (i\gamma\pi/4)(1 + P_{00})} \\ A_n^{(0)} &= \frac{1}{1 + P_{nn}} \left\{ \left(1 - \frac{1}{i\gamma} \sqrt{\frac{2}{\pi}} A_0^{(0)} \right) \right. \\ &\quad \left. \times 2\sqrt{\frac{2}{\pi}} X_{n0} - \sum_{m=0}^{n-1} P_{nm} A_m^{(0)} \right\} \quad (n \geq 1) \end{aligned} \right\} \quad (3.15)$$

and

$$\left. \begin{aligned} A_0^{(q)} &= -\frac{i\gamma\pi}{4} \frac{1}{X_{00} + (i\gamma\pi/4)(1 + P_{00})} \\ &\quad \times \sum_{m=1}^q P_{0m} A_m^{(q-m)} \\ A_n^{(q)} &= \frac{1}{1 + P_{nn}} \left\{ \frac{i4}{\gamma\pi} A_0^{(q)} X_{n0} \right. \\ &\quad \left. - \sum_{m=0}^{n-1} P_{nm} A_m^{(q)} - \sum_{m=1}^q P_{n,n+m} A_{n+m}^{(q-m)} \right\}, \end{aligned} \right\} \quad (3.16)$$

$$(n \geq 1)$$

These are calculated successively from the lower level of the approximation to the higher one. We obtained A_0, A_1, A_2 and A_3 up to the fourth, third, second and first term, respectively. a_s is obtained from (3.7). Particularly, the important coefficient a_0 is given by

$$a_0 = 1 + i\sqrt{\frac{2}{\pi}} \frac{1}{\gamma} A_0. \quad (3.17)$$

The values of A_n ($n=0, 1, 2, 3$) and a_0 for several values of γ are shown in Table I. Substituting these values back into the equation (3.8), we see that they satisfies (3.8) to the degree sufficient for a practical purposes.

When γ is sufficiently small, it is convenient to use a power expansion

$$A_n = \alpha_{n1}\gamma + \alpha_{n2}\gamma^2 + \cdots \quad (3.18)$$

Substituting power expansions

$$G_{nl} = (4n+1) \frac{\sqrt{\pi}}{2}$$
$$\times \left[\left(\frac{\gamma}{2} \right)^{2|n-l|} \sum_{\mu=0}^{\infty} \frac{(-1)^{|n-l|+\mu} \Gamma(2|n-l|+2\mu+1) \Gamma'(n+l-|n-l|+\frac{1}{2}-\mu) (\gamma/2)^{2\mu}}{\mu! \Gamma(\frac{1}{2}-|n-l|-\mu) \Gamma'(|n-l|+\mu+1) \Gamma'(2|n-l|+\mu+1) \Gamma(n+l+|n-l|+\mu+\frac{3}{2})} \right.$$
$$\left. - i \left(\frac{\gamma}{2} \right)^{2n+2l+1} \sum_{\mu=0}^{\infty} \frac{(-1)^\mu \Gamma(2n+2l+2\mu+2) \Gamma'(n+l+\mu+1) (\gamma/2)^{2\mu}}{\mu! \Gamma(2n+2l+\mu+2) \Gamma(2n+\mu+\frac{3}{2}) \Gamma(2l+\mu+\frac{3}{2}) \Gamma(n+l+\mu+\frac{3}{2})} \right] \quad (3.19)$$

and

$$Q_{ln} \equiv (4l+1) \sum_{s=1}^{\infty} \frac{2J_{2l+\frac{1}{2}}(\beta_s) J_{2n+\frac{1}{2}}(\beta_s)}{\beta_s \sqrt{\beta_s^2 - \gamma^2} [J_0(\beta_s)]^2} = \sum_{m=0}^{\infty} Q_{ln}^{(2m)} \gamma^{2m} \quad (3.20)$$

where

$$Q_{ln}^{(2m)} = (4l+1) \frac{\Gamma(m+\frac{1}{2})}{\Gamma(\frac{1}{2})m!} \sum_{s=1}^{\infty} \frac{2J_{2l+\frac{1}{2}}(\beta_s) J_{2n+\frac{1}{2}}(\beta_s)}{\beta_s^{2+2m} [J_0(\beta_s)]^2} \quad (3.21)$$

in (3.8) and comparing the terms of the same power of γ , we have the following equations

$$\left. \begin{aligned} 1 - \frac{1}{i} \sqrt{\frac{2}{\pi}} \alpha_{01} &= 0, \quad \sum_{n=1}^{\infty} (\delta_{ln} + Q_{ln}^{(0)}) \alpha_{n1} = -Q_{l0}^{(0)} \alpha_{01}, \\ i \frac{4}{\pi} \alpha_{02} &= (1 + Q_{00}^{(0)}) \alpha_{01} + \sum_{n=1}^{\infty} Q_{0n}^{(0)} \alpha_{n1}, \quad \sum_{n=1}^{\infty} (\delta_{ln} + Q_{ln}^{(0)}) \alpha_{n2} = -Q_{l0}^{(0)} \alpha_{02} \\ &\dots\dots\dots \\ &\dots\dots\dots \end{aligned} \right\} \quad (3.22)$$

and obtain

$$\left. \begin{aligned} \alpha_{01} &= i \sqrt{\frac{\pi}{2}} \\ \alpha_{n1} &= - \left\{ \sum_{m=1}^{\infty} [(E + Q')^{-1}]_{nm} Q_{m0}^{(0)} \right\} \alpha_{01} \\ \alpha_{02} &= \frac{1}{i} \frac{\pi}{4} \left\{ 1 + Q_{00}^{(0)} - \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} Q_{0n} [(E + Q')^{-1}]_{nm} Q_{m0} \right\} \alpha_{01} \\ \alpha_{n2} &= - \left\{ \sum_{m=1}^{\infty} [(E + Q')^{-1}]_{nm} Q_{m0}^{(0)} \right\} \alpha_{02} \\ &\dots\dots\dots \\ &\dots\dots\dots \end{aligned} \right\} \quad (3.23)$$

where E is the unit matrix and $(E + Q')^{-1}$ the inverse of the matrix $E + Q'$, of which the elements are defined for m and n larger than 0, i.e.

$$[E + Q']_{mn} = \delta_{mn} + Q_{mn}^{(0)} \quad (m, n \geq 1)$$

§ 4. Field at Large Distances

The behavior of the solution at large distances depends on the properties of the S_n , defined by (2.4), for large $R = \sqrt{r^2 + z^2}$. We first consider the function $\psi(r)$ defined by

$$\left. \begin{aligned} \psi(r) &= S_n \left(\frac{r}{a}, z \right) \quad z > 0 \\ &= S_n \left(\frac{r}{a}, -z \right) \quad z < 0. \end{aligned} \right\} \quad (4.1)$$

When $z=0$, $\partial\psi/\partial z$ reduces to Weber-Schafheitlin's integral, and vanishes for $r > a$. Thus the discontinuity of $\partial\psi/\partial z$ lies only on the circular plate $z=0$, $r < a$. We denote a surface which envelops this circular plate by S . According to Green's theorem, we obtain

$$\begin{aligned} \psi(r) &= \frac{1}{4\pi} \iint_S \left\{ \frac{\exp(-ikR')}{R'} \frac{\partial\psi}{\partial n} \right. \\ &\quad \left. - \psi \frac{\partial}{\partial n} \frac{\exp(-ikR')}{R'} \right\} dS \end{aligned} \quad (4.2)$$

where $R' = |r - r'|$ and r' represents the point on S . The contribution from the surface at infinity vanishes on account of the property of S_n ⁵⁾ that the magnitude of S_n is of the order of $1/R$ for large R . The integrals of the second term over the surface above and

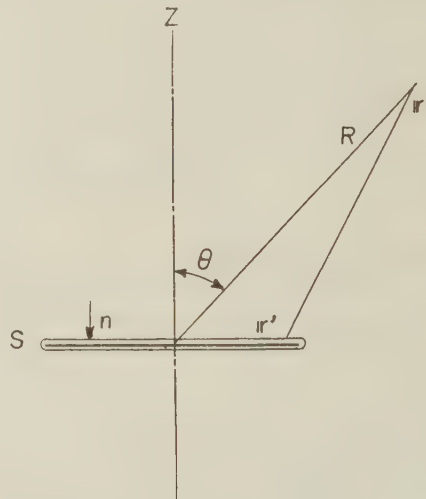


Fig. 2.

below the circular plate cancel each other, for ψ has the same value on both sides of the plate.

When R is large, R' can be expanded in power series of $1/R$ and the first two terms are expressed as follows

$$R' = \sqrt{R^2 - 2Rr' \sin \theta \cos(\varphi - \varphi') + r'^2}$$

$$= R \left\{ 1 - \frac{r'}{R} \sin \theta \cos(\varphi - \varphi') + 0 \left(\frac{1}{R^2} \right) \right\}$$

where θ is the angle between r and z -axis, and φ, φ' the azimuthal angles. Neglecting the term of the order of $1/R^2$ and of higher order in (4.2), we have

$$\begin{aligned}
\phi(r) &\sim -\frac{1}{2\pi} \frac{\exp(ikR)}{R} \int_0^{2\pi} d\varphi' \int_0^a r' dr' \exp\{ikr' \sin \theta \cos(\varphi - \varphi')\} \left\{ \left(\frac{\partial \phi}{\partial z} \right)_{z=0} \right\} \\
&= \frac{\exp(-ikR)}{2\pi a R} \int_0^{2\pi} d\varphi' \int_0^a r' dr' \exp\{ikr' \sin \theta \cos(\varphi - \varphi')\} \int_0^\infty \sqrt{\xi} J_0\left(\frac{r'\xi}{a}\right) J_{2n+\frac{1}{2}}(\xi) d\xi \\
&= \frac{\exp(-ikR)}{aR} \int_0^a J_0(kr' \sin \theta) r' dr' \int_0^\infty \sqrt{\xi} J_0\left(\frac{r'\xi}{a}\right) J_{2n+\frac{1}{2}}(\xi) d\xi \\
&= \frac{a \exp(-ikR)}{\sqrt{2} \Gamma(n+\frac{1}{2}) R} \int_0^1 J_0(ka\sqrt{x} \sin \theta) \frac{d^n}{dx^n} \{x^n (1-x)^{n-\frac{1}{2}}\} dx \\
&= \sqrt{\frac{2}{\pi}} a j_{2n}(r \sin \theta) \frac{\exp(-ikR)}{R}.
\end{aligned} \tag{4.3}$$

Then as the asymptotic form of ϕ_2 , we have

$$\phi_2\left(\frac{r}{a}, a\right) \sim \sqrt{\frac{2}{\pi}} \frac{a V_0}{k} \sum_{n=0}^{\infty} A_n j_{2n}(r \sin \theta) \frac{\exp\left(-ir \frac{R}{a}\right)}{R}. \tag{4.4}$$

§ Calculation of the Physical Quantities

Using the values in Table I, we can calculate various physical quantities for the corresponding values of r .

a) Acoustic impedance

Acoustic impedance per unit area of the pipe is defined by

$$Z \equiv r + ix = p_m / v_m \tag{5.1}$$

where p_m and v_m are the mean values of pressure and velocity at the open end, respectively, and given by

$$\begin{aligned}
p_m &= \frac{1}{\pi a^2} \int_0^{2\pi} d\varphi \int_0^a \left\{ i\omega \rho \phi\left(\frac{r}{a}, 0\right) \right\} r dr \\
&= i\rho c V_0 (1 + a_0) \\
v_m &= \frac{1}{\pi a^2} \int_0^{2\pi} d\varphi \int_0^a \left\{ -\frac{\partial}{\partial z} \phi\left(\frac{r}{a}, 0\right) \right\} r dr \\
&= iV_0 (1 - a_0)
\end{aligned} \tag{5.2}$$

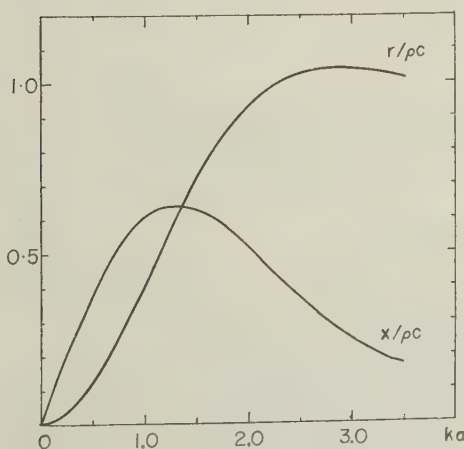


Fig. 3. Acoustic resistance and reactance, as functions of $ka = 2\pi a/\lambda$.

where ρ is the density of the fluid and c the velocity of the sound propagation. Then we have

$$\begin{aligned}
\frac{p_m}{v_m} &= \rho c \frac{1 + a_0}{1 - a_0}, \\
r &= \rho c \frac{1 - |a_0|^2}{|1 - a_0|^2},
\end{aligned} \tag{5.4}$$

$$x = \rho c \frac{2 \operatorname{Im} a_0}{|1 - a_0|^2}. \tag{5.5}$$

The dependence of these quantities on $r = ka$ is shown in Fig. 3.

b) Power gain function

The time average of the energy flow per unit area can be written

$$\operatorname{Re} \frac{i\rho c k}{2} (\bar{\phi} \nabla \phi).$$

When $R \gg a$, the energy $P(\theta)$ radiated into the unit solid angle in the direction θ is given by

$$\begin{aligned}
P(\theta) &= \operatorname{Re} \lim_{R \rightarrow \infty} R^2 \frac{i\rho c k}{2} \bar{\phi}_2 \frac{\partial}{\partial R} \phi_2 \\
&= \frac{\rho c a^2}{\pi} V_0^2 \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \bar{A}_n A_{n'} j_{2n}(r \sin \theta) \\
&\quad \times j_{2n'}(r \sin \theta),
\end{aligned} \tag{5.6}$$

where we used the asymptotic form (4.4) in section 4. The total radiation energy P_r is written

$$\begin{aligned}
P_r &= \int_0^{2\pi} d\varphi \int_0^{\pi/2} P(\theta) \sin \theta d\theta \\
&= \frac{\pi \rho c a V_0^2}{k} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \bar{A}_n A_{n'} \\
&\quad \times \int_0^\gamma \frac{J_{2n+\frac{1}{2}}(\xi) J_{2n'+\frac{1}{2}}(\xi)}{\sqrt{\gamma^2 - \xi^2}} d\xi.
\end{aligned}$$

Comparing the form of the integral in the double summation to the definition of G_{nm} (3.2), and taking the symmetric property of the integral regarding n, n' into consideration, we obtain the following expression

$$P_r = \frac{\pi \rho c a V_0^2}{k} \operatorname{Im} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \frac{1}{4n'+1} \bar{A}_n \bar{G}_{nm'} A_{n'}.$$

When we express the above equation by a_s instead of A_n using (3.7) and (3.8), it turns out that the contribution to the imaginary part comes only from a_0 , and we have

$$P_r = \frac{\rho c \pi a^2 V_0^2}{2} (1 - |a_0|^2). \quad (5.7)$$

Then the relation between P_r and acoustic resistance r is written

$$P_r = \frac{\pi a^2}{2} |v_m|^2 r. \quad (5.8)$$

Power gain function $g(\theta)$ is given by

$$\begin{aligned} g(\theta) &= \frac{P(\theta)}{P_r/4\pi} \\ &= \frac{8}{\pi(1 - |a_0|^2)} \\ &\times \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \bar{A}_n A_{n'} j_{2n}(\gamma \sin \theta) j_{2n'}(\gamma \sin \theta). \end{aligned} \quad (5.9)$$

The dependence of $g(\theta)$ on γ is shown in Fig. 4.

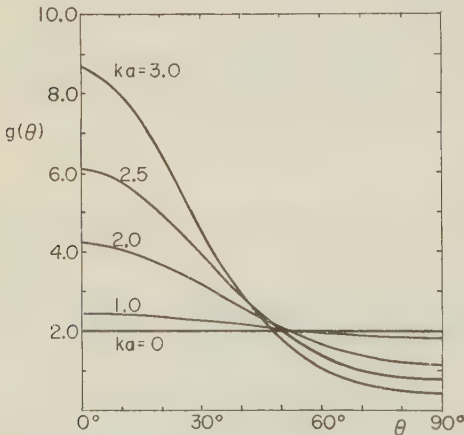


Fig. 4. The dependence of the power gain function on angle for various values of ka .

c) Transmission coefficient t

Transmission coefficient t is defined by the ratio of the total radiation energy P_r to the incident energy P_i ,

$$t \equiv \frac{P_r}{P_i} = 1 - |a_0|^2. \quad (5.10)$$

The dependence of t on γ is shown in Fig. 6.

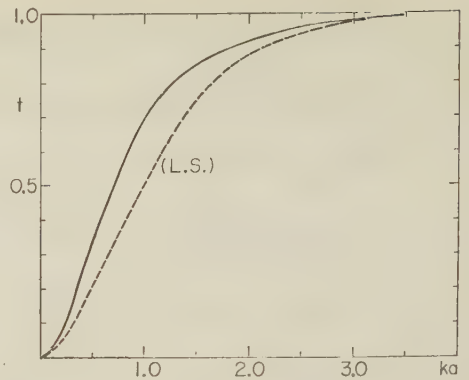


Fig. 5. The transmission coefficient as a function of ka . The dashed curve represents the value in case of an unflanged pipe (by Levine & Schwinger).

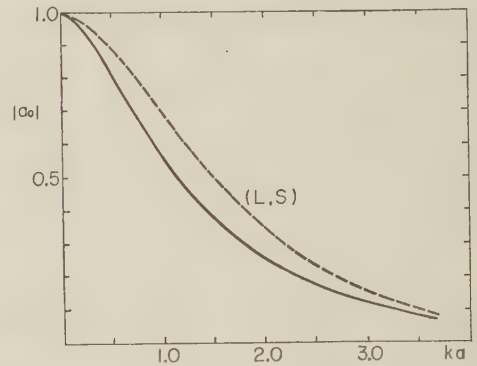


Fig. 6. The reflection coefficient as a function of ka . The dashed curve represents the unflanged value (by L. & S.).

d) The end correction

For the values of γ which is smaller than β_1 , the field within the pipe far from the open end is almost determined by the term

$$\frac{V_0}{k} \left\{ \exp\left(-\frac{i\gamma z}{a}\right) + a_0 \exp\left(\frac{i\gamma z}{a}\right) \right\}. \quad (5.11)$$

The field represented by (5.11) has the velocity maximum or the pressure minimum at $z=l$, where the length l is defined by

$$a_0 = -|a_0| \exp(-i2kl) \quad (5.12)$$

or explicitly

$$\frac{l}{a} = \frac{1}{2\gamma} \tan^{-1} \left(-\frac{\operatorname{Im} a_0}{\operatorname{Re} a_0} \right). \quad (5.13)$$

Further, when γ is small, a_0 tends to -1 , i.e. the perfect reflection occurs and the velocity potential within the pipe is the same as if the pipe were lengthened by l and the open end behaved as a loop. $\operatorname{Im} a_0$ is of the first order in γ , and (5.13) gives the finite

value of the end correction in the limit $r \rightarrow 0$. From (3.17) and (3.18) we have

$$a_0 = -1 + i2\sqrt{\frac{2}{\pi}}\alpha_{02}r + O(r^2). \quad (5.14)$$

Then we obtain

$$\begin{aligned} \delta &= \lim_{r \rightarrow 0} \frac{l}{a} = \sqrt{\frac{2}{\pi}}\alpha_{02} \\ &= \frac{\pi}{4} \left\{ 1 + Q_{00}^{(0)} - \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} Q_{0m}^{(0)} [(E+Q')^{-1}]_{mn} Q_{n0}^{(0)} \right\}. \end{aligned} \quad (5.15)$$

Neglecting the elements $Q_{mn}^{(0)}$ with m or n larger than p , we have the approximate values of $[(E+Q')^{-1}]$ and then δ_p , i.e.

$$\begin{aligned} \delta_2 &= 0.822482, \quad \delta_3 = 0.822013, \quad \delta_4 = 0.821850, \\ \delta_5 &= 0.821778. \end{aligned} \quad (5.16)$$

The limit value δ , extrapolated from the above values is

$$\delta = \lim_{p \rightarrow \infty} \delta_p = 0.8217. \quad (5.17)$$

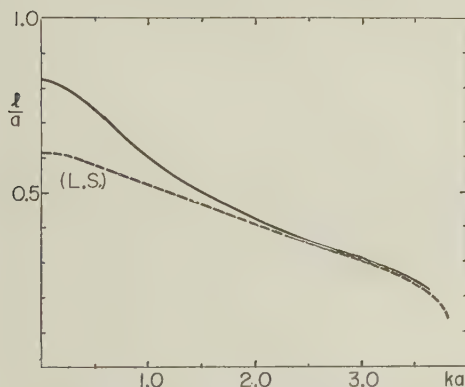


Fig. 7. The end correction as a function of ka .

The dashed curve represents the unflanged value (by L. & S.).

§6. Discussions

We solved the problem in case where $r (=ka)$ is smaller than the value $\beta_1 = 3.8317$ that corresponds to the first resonance wave length,* and calculated the impedance, power gain function, transmission coefficient and end correction which is shown in Figs. 3 to 7. For the purpose of comparison, some of the results obtained by H. Levine and

J. Schwinger in case of the unflanged pipe are shown by dashed curves. The transmission coefficient is converted from their reflection coefficient given in reference 1). The flanged pipe, about 1.34 times at $ka = 1.00$.

As for the end correction in the long wave limit, Lord Rayleigh⁸⁾ considered the two cases where the open end has an infinitely thin disc of perfect conductivity and an infinitely thin piston, the effect of which will be to decrease and increase the effective length of the tube, respectively. It is easily shown that these modified problems give the end corrections $\delta_1 = \pi/4$ and $\delta_2 = 8\pi/3$.

Therefore the true end correction δ must satisfy the following relation

$$\pi/4 < \delta < 8\pi/3, \quad \text{i.e. } 0.785 < \delta < 0.849. \quad (6.1)$$

Further, in a variational approximation, he showed that δ is not greater than 0.82422. He expected that the right value is "probably about" 0.82. Our theory leads to $\delta = 0.8217$, ascertaining his expectation. According to H. Levine and J. Schwinger, the end correction δ' in case of the unflanged pipe is

$$\delta' = 0.6133 \quad (6.2)$$

a little smaller than the value of the flanged pipe. It is expected that as the wave number increases, the influence of the flange upon the diffraction becomes smaller. Indeed, as shown in Fig. 7, the end corrections in both cases are nearly equal for the values of ka about 3.

References

- 1) H. Levine and J. Schwinger: Phys. Rev. **73** (1948) 383.
- 2) H. Levine and J. Schwinger: *ibid.* **73** (1948), 393.
- 3) G. N. Watson: *Theory of Bessel Functions* (Cambridge, 1922) 398.
- 4) I. Kobayashi: Sci. Rep. Tohoku Imp. Univ. (1) **20** (1931) 197.
- 5) Y. Nomura and S. Katsura: J. Phys. Soc. Japan **10** (1955) 285.
- 6) Y. Nomura: Rep. Res. Inst. Elect. Comm. Tohoku Univ. **5** (1953) 203.
- 7) Y. Nomura and S. Katsura: Rep. Res. Inst. Elect. Comm. Tohoku Univ. **10** (1958) 1.
- 8) Lord Rayleigh (J. W. Strutt): *Theory of Sound* vol. II 182, 197 and Appendix A. (London, 1926).

* In case $ka > \beta_1$, where more than one progressive mode can exist in the pipe, an appropriate modification of the theory is required.

Measures of Finite Strain and Stress-Strain Relations

By Wataru SEGAWA

College of Humanities and Sciences, Nihon University, Tokyo

(Received September 10, 1959)

Ordinarily, stress-strain relation of Lagrange's representation is written in terms of Lagrange's representation of stress σ^{ij} and the Love measure e_{ij}^L . From the above relation, we can derive Reiner's equation in terms of Euler's representation of stress $T^{\lambda\mu}$ and the Green measure $e_{\lambda\mu}^G$.

In this paper, it is shown that σ^{ij} and e_{ij} defined by

$$\sigma^{ij} = D x_{,i}^{*\lambda} x_{,j}^{*\mu} T^{\lambda\mu}, \quad e_{ij} = \frac{1}{2}(\delta_{ij} - g^{ij})$$

can play the role of σ^{ij} and e_{ij}^L and starting from stress-strain relation of σ^{ij} and e_{ij} , we arrive at Reiner's equation in terms of $T^{\lambda\mu}$ and the Almansi measure $e_{\lambda\mu}^A$.

Various relations relating to four measures above mentioned and to their first variations are also shown, as well as various relations among different strain invariants.

§ 1. Introduction

Many measures of finite strain have been utilized so far,¹⁾²⁾ but, as far as we know, they are Euler's representation of strain except the Love measure e_{ij}^L , the Euler's representation of which is the Almansi measure $e_{\lambda\mu}^A$.³⁾ In this paper, we will discuss how another measure of Lagrange's representation e_{ij} , Euler's representation of which is the Green measure $e_{\lambda\mu}^G$, can be utilized, and will also discuss some properties of four measures above-mentioned for the comparison.

Stress-strain relation in Lagrange's representation is usually expressed by the stress in Lagrange's representation σ^{ij} and the Love Measure e_{ij}^L , from which we can derive stress-strain relation in Euler's representation. If the material is isotropic before deformation, the latter relation becomes equivalent to Rivlin's equation.⁴⁾ As it will be shown later, Rivlin's equation can be converted into Reiner's equation¹⁾⁵⁾ which is expressed by Euler's representation of stress $T^{\lambda\mu}$ and Green measure $e_{\lambda\mu}^G$.

$T^{\lambda\mu}$ is equivalent to actual stress, stress per unit area after the deformation, but σ^{ij} is not equivalent to conventional stress, stress per unit area before the deformation and is not, strictly speaking, stress⁶⁾. In this paper, we shall use another stress in Lagrange's representation σ^{ij} which also is not, strictly speaking, stress. Then, as we shall see later, we can derive stress-strain relation in terms of σ^{ij} and e_{ij} and subsequently in terms of $T^{\lambda\mu}$

and $e_{\lambda\mu}^A$.

Various relations existing among different strain invariants will be also shown, as well as the behaviors of variation tensors of strains.

§ 2. Definitions of e_{ij}^L , $e_{\lambda\mu}^A$, e_{ij} and $e_{\lambda\mu}^G$

Let us denote the quantities relating to Lagrange's and Euler's representation by the suffixes of Latin letters (i, j, k , etc.) and of Greek letters (λ, μ, ν , etc.), respectively.

Let the position of a material point be x^i ($i=1, 2, 3$) for undeformed state ($T=0$) and x^{*i} ($i=1, 2, 3$) for deformed state ($T=t$), respectively, on a rectangular coordinate system X^i ($i=1, 2, 3$) fixed in space. Let the time t be fixed. We assume that the coordinates x^{*i} are single-valued and continuously differentiable functions of the x^i and vice versa. Then, we can define four kinds of symmetric tensors, each of whose components is a summation of the quadratic products of coordinate gradients, as follows.

$$g_{ij} = x_{,i}^{*k} x_{,j}^{*k} \quad (x_{,i}^{*k} = \partial x^{*k} / \partial x^i) \quad (2.1)$$

$$g'_{\lambda\mu} = x_{,\lambda}^k x_{,\mu}^k \quad (x_{,\lambda}^k = \partial x^k / \partial x^{*\lambda}) \quad (2.2)$$

$$g^{ij} = x_{,i}^k x_{,j}^k \quad (x_{,i}^k = \partial x^k / \partial x^{*i}) \quad (2.3)$$

$$g'^{\lambda\mu} = x^{*\lambda}_{,k} x^{*\mu}_{,k} \quad (x^{*\lambda}_{,k} = \partial x^{*\lambda} / \partial x^k) \quad (2.4)$$

where we have used Einstein's convention which will be used throughout this article. From the above equations, we can readily prove that

$$g_{ik} g^{jk} = \delta_{ij} \quad (2.5)$$

$$g'_{\lambda\nu} g'^{\nu\mu} = \delta_{\lambda\mu} \quad (2.6)$$

where δ_{ij} and $\delta_{\lambda\mu}$ are Kronecker's delta. As is well-known, g_{ij} and g^{ij} are the covariant and the contravariant components of fundamental tensor, respectively.⁶⁾

From Eq. (2.1)—Eq. (2.4) and Kronecker's delta, we can constitute four measures of finite strain as follows:

$$e_{ij}^L = \frac{1}{2}(g_{ij} - \delta_{ij}) \quad (2.7)$$

$$e_{\lambda\mu}^A = \frac{1}{2}(g_{\lambda\mu} - g'^{\lambda\mu}) \quad (2.8)$$

$$e_{ij} = \frac{1}{2}(\delta_{ij} - g^{ij}) \quad (2.9)$$

$$e_{\lambda\mu}^G = \frac{1}{2}(g'^{\lambda\mu} - \delta_{\lambda\mu}) \quad (2.10)$$

e_{ij}^L defined by Eq. (2.7) is equivalent to the Love measure ordinarily used, except for the factor 1/2 in the shear components, and $e_{\lambda\mu}^A$ is tensor expression of the Almansi measure.³⁾ We can easily prove that $e_{\lambda\mu}^G$ defined by Eq. (2.10) is a tensor expression of the Green measure. The three measures above-mentioned are prevailing, but e_{ij} is not so, in spite of its simple composition.

From the above equations, we can easily prove that

$$e_{ij}^L x_{,\lambda}^i x_{,\mu}^j = e_{\lambda\mu}^A \quad \text{or} \quad e_{ij}^L = x_{,\lambda}^* x_{,\mu}^* e_{\lambda\mu}^A \quad (2.11)$$

$$e_{ij} x_{,\lambda}^* x_{,\mu}^* = e_{\lambda\mu}^G \quad \text{or} \quad e_{ij} = x_{,\lambda}^i x_{,\mu}^j e_{\lambda\mu}^G \quad (2.12)$$

It is noticeable that the transformation between e_{ij}^L and $e_{\lambda\mu}^A$ is covariant, as it is well-known, but e_{ij} and $e_{\lambda\mu}^G$ transform with each other as contravariant tensor.

§ 3. Invariants of Strains

Let us appoint, for the latter use, three sets, each of which consists of three invariant quantities, to each of our measures as follows:

$$\text{i) } e_{ij}^L \quad I_L = e_{ii}^L, \quad II_L = \frac{1}{2} e_{ij}^L e_{ij}^L, \quad III_L = \frac{1}{6} e_{ij}^L e_{jk}^L e_{ki}^L \quad (3.1)$$

$$\left. \begin{aligned} I_L' &= g_{ij} \\ II_L' &= g_{22}g_{33} + g_{33}g_{11} + g_{11}g_{22} - g_{23}g_{32} \\ &\quad - g_{31}g_{13} - g_{12}g_{21} \end{aligned} \right\} \quad (3.2)$$

$$\left. \begin{aligned} III_L' &= \det |g_{ij}| \\ I_L'' &= e_{ii}^L \\ II_L'' &= e_{22}^L e_{33}^L + e_{33}^L e_{11}^L + e_{11}^L e_{22}^L - e_{23}^L e_{32}^L \\ &\quad - e_{13}^L e_{31}^L - e_{12}^L e_{21}^L \end{aligned} \right\} \quad (3.3)$$

$$III_L'' = \det |e_{ij}^L|$$

$$\text{ii) } e_{\lambda\mu}^A \quad I_A = e_{\lambda\lambda}^A, \quad II_A = \frac{1}{2} e_{\lambda\mu}^A e_{\lambda\mu}^A, \quad III_A = \frac{1}{6} e_{\lambda\mu}^A e_{\mu\nu}^A e_{\nu\lambda}^A \quad (3.4)$$

$$\left. \begin{aligned} I_A' &= g'_{\lambda\lambda} \\ II_A' &= g'_{22}g'_{33} + g'_{33}g'_{11} + g'_{11}g'_{22} - g'_{23}g'_{32} \\ &\quad - g'_{31}g'_{13} - g'_{12}g'_{21} \end{aligned} \right\} \quad (3.5)$$

$$\left. \begin{aligned} III_A' &= \det |g'_{\lambda\mu}| \\ I_A'' &= e_{\lambda\lambda}^A \\ II_A'' &= e_{22}^A e_{33}^A + e_{33}^A e_{11}^A + e_{11}^A e_{22}^A - e_{23}^A e_{32}^A \\ &\quad - e_{31}^A e_{13}^A - e_{12}^A e_{21}^A \end{aligned} \right\} \quad (3.6)$$

$$\text{iii) } e_{ij} \quad I = e^{ii}, \quad II = \frac{1}{2} e_{ij} e_{ij}, \quad III = \frac{1}{6} e_{ij} e_{jk} e_{ki} \quad (3.7)$$

$$\left. \begin{aligned} I' &= g^{ii} \\ II' &= g^{22}g^{33} + g^{33}g^{11} + g^{11}g^{22} - g^{23}g^{32} \\ &\quad - g^{31}g^{13} - g^{12}g^{21} \end{aligned} \right\} \quad (3.8)$$

$$\left. \begin{aligned} III' &= \det |g^{ij}| \\ I' &= e_{ii} \\ II' &= e_{22}e_{33} + e_{33}e_{11} + e_{11}e_{22} - e_{23}e_{32} \\ &\quad - e_{31}e_{13} - e_{12}e_{21} \end{aligned} \right\} \quad (3.9)$$

$$\text{iv) } e_{\lambda\mu}^G \quad I_G = e_{\lambda\lambda}^G, \quad II_G = \frac{1}{2} e_{\lambda\mu}^G e_{\lambda\mu}^G, \quad III_G = \frac{1}{6} e_{\lambda\mu}^G e_{\mu\nu}^G e_{\nu\lambda}^G \quad (3.10)$$

$$\left. \begin{aligned} I_G' &= g'^{\lambda\lambda} \\ II_G' &= g'^{22}g'^{33} + g'^{33}g'^{11} + g'^{11}g'^{22} \\ &\quad - g'^{23}g'^{32} - g'^{31}g'^{13} - g'^{12}g'^{21} \end{aligned} \right\} \quad (3.11)$$

$$\left. \begin{aligned} III_G' &= \det |g'^{\lambda\mu}| \\ I_G'' &= e_{\lambda\lambda}^G \\ II_G'' &= e_{22}^G e_{33}^G + e_{33}^G e_{11}^G + e_{11}^G e_{22}^G - e_{23}^G e_{32}^G \\ &\quad - e_{31}^G e_{13}^G - e_{12}^G e_{21}^G \end{aligned} \right\} \quad (3.12)$$

$$III_G'' = \det |e_{\lambda\mu}^G|$$

Using the above definition, together with Eq. (2.5) and Eq. (2.6), we can easily prove that the following relations hold:

$$\left. \begin{aligned} I_L &= \frac{1}{2}(I_L' - 3) \\ II_L &= \frac{1}{2} \frac{1}{3}(I_L' - 3)^2 - \frac{1}{4}(II_L' - 3) + \frac{1}{2}(I_L' - 3) \\ III_L &= \frac{1}{6} \frac{1}{3}(I_L' - 3)^3 + \frac{1}{8}\{I_L' - 3 - (II_L' - 3) \\ &\quad + III_L' - 1\} - \frac{1}{2}(I_L' - 3)\{\frac{1}{4}(II_L' - 3) \\ &\quad - \frac{1}{2}(I_L' - 3)\} \end{aligned} \right\} \quad (3.13)$$

$$\left. \begin{aligned} I_L'' &= I_L \\ II_L'' &= \frac{1}{2}(L_L)^2 - II_L \\ III_L'' &= III_L - I_L II_L + \frac{1}{6}(I_L)^3 \end{aligned} \right\} \quad (3.14)$$

$$\left. \begin{aligned} -I_A &= \frac{1}{2}(I_A' - 3) \\ II_A &= \frac{1}{24}(I_A' - 3)^2 - \frac{1}{4}(II_A' - 3) \\ &\quad + \frac{1}{2}(I_A' - 3) \\ -III_A &= \frac{1}{8}(I_A' - 3)^3 + \frac{1}{8}\{I_L' - 3 - (II_A' - 3) \\ &\quad + III_A' - 1\} - \frac{1}{2}(I_A' - 3)\{\frac{1}{4}(II_A' - 3) \\ &\quad - \frac{1}{2}(I_A' - 3)\} \end{aligned} \right\} \quad (3.15)$$

$$\left. \begin{aligned} I_A'' &= I_A \\ II_A'' &= \frac{1}{2}(I_A)^2 - II_A \\ III_A'' &= III_A - I_A II_A + \frac{1}{6}(I_A)^3 \end{aligned} \right\} \quad (3.16)$$

$$\left. \begin{aligned} -I &= \frac{1}{2}(I' - 3) \\ II &= \frac{1}{24}(I' - 3)^2 - \frac{1}{4}(II' - 3) + \frac{1}{2}(I' - 3) \\ -III &= \frac{1}{8}(I' - 3)^3 + \frac{1}{8}\{I' - 3 - (II' - 3) \\ &\quad + III' - 1\} - \frac{1}{2}(I' - 3)\{\frac{1}{4}(II' - 3) \\ &\quad - \frac{1}{2}(I' - 3)\} \end{aligned} \right\} \quad (3.17)$$

$$\left. \begin{aligned} I'' &= I \\ II'' &= \frac{1}{2}(I)^2 - II \\ III'' &= III - I II + \frac{1}{6}(I)^3 \end{aligned} \right\} \quad (3.18)$$

$$\left. \begin{aligned} I_G &= \frac{1}{2}(I_G' - 3) \\ II_G &= \frac{1}{24}(I_G' - 3)^2 - \frac{1}{4}(II_G' - 3) + \frac{1}{2}(I_G' - 3) \\ III_G &= \frac{1}{8}(I_G' - 3)^3 + \frac{1}{8}\{I_G' - 3 - (II_G' - 3) \\ &\quad + III_G' - 1\} - \frac{1}{2}(I_G' - 3)\{\frac{1}{4}(II_G' - 3) \\ &\quad - \frac{1}{2}(I_G' - 3)\} \end{aligned} \right\} \quad (3.19)$$

$$\left. \begin{aligned} I_G'' &= I_G \\ II_G'' &= \frac{1}{2}(I_G)^2 - II_G \\ III_G'' &= III_G - I_G II_G + \frac{1}{6}(I_G)^3 \end{aligned} \right\} \quad (3.20)$$

$$I_L = I_G, \quad II_L = II_G, \quad III_L = III_G \quad (3.21)$$

$$I_L' = I_G', \quad II_L' = II_G', \quad III_L' = III_G' \quad (3.22)$$

$$I_L'' = I_G'', \quad II_L'' = II_G'', \quad III_L'' = III_G'' \quad (3.23)$$

$$I = I_A, \quad II = II_A, \quad III = III_A \quad (3.24)$$

$$I' = I_A', \quad II' = II_A', \quad III' = III_A' \quad (3.25)$$

$$I'' = I_A'', \quad II'' = II_A'', \quad III'' = III_A'' \quad (3.26)$$

$$I_L' = II'/III', \quad II_L' = I'/III', \quad III_L' = 1/III' \quad (3.27)$$

$$I_A' = II_G'/III_G', \quad II_A' = I_G'/III_A', \quad III_A' = 1/II_G' \quad (3.28)$$

§ 4. Variations of Strains

When we want to derive the variations of strains, we should regard the initial position x^i as constant, because, in this case, independent variables are x^i and time t and the variations are related to t . Thus, from Eq. (2.1)—Eq. (2.4) and Eq. (2.7)—Eq. (2.10), we have

$$\delta e_{ij}^L = \frac{1}{2}\{(\delta x^{*k})_{,i} x_{,j}^{*k} + (\delta x^{*k})_{,j} x_{,i}^{*k}\} \quad (4.1)$$

$$\delta e_{\lambda\mu}^A = \frac{1}{2}\{(\delta x^{*k})_{,\lambda} x_{,\mu}^{*k} + (\delta x^{*k})_{,\mu} x_{,\lambda}^{*k}\} \quad (4.2)$$

$$\delta e_{ij} = \frac{1}{2}\{(\delta x^{*\alpha})_{,i} x_{,j}^{*\alpha} + (\delta x^{*\beta})_{,j} x_{,i}^{*\beta}\} \quad (4.3)$$

$$\delta e_{\lambda\mu}^G = \frac{1}{2}\{(\delta x^{*\lambda})_{,\kappa} x_{,\kappa}^{*\mu} + (\delta x^{*\mu})_{,\kappa} x_{,\kappa}^{*\lambda}\} \quad (1.4)$$

where we have used following relations:

$$\delta(x_{,j}^{*k}) = (\gamma x^{*k})_{,j} \text{ etc.} \quad (4.5)$$

$$\delta(x_{,\lambda}^{*k}) = -(\delta x^{*\alpha})_{,\lambda} x_{,\alpha}^{*k} \text{ etc.} \quad (4.6)$$

Let us define $\delta\epsilon_{\lambda\mu}$ by

$$\delta\epsilon_{\lambda\mu} = \frac{1}{2}\{(\delta x^{*\lambda})_{,\mu} + (\delta x^{*\mu})_{,\lambda}\} \quad (4.7)$$

then, from Eq. (4.1) and Eq. (4.3), we can derive following relations:

$$\delta e_{ij}^L x_{,\lambda}^{*i} x_{,\mu}^{*j} = \delta\epsilon_{\lambda\mu} \text{ or } \delta e_{ij}^L = x_{,\lambda}^{*i} x_{,\mu}^{*j} \delta\epsilon_{\lambda\mu} \quad (4.8)$$

$$\delta e_{ij} x_{,\lambda}^{*i} x_{,\mu}^{*j} = \delta\epsilon_{\lambda\mu} \text{ or } \delta e_{ij} = x_{,\lambda}^{*i} x_{,\mu}^{*j} \delta\epsilon_{\lambda\mu} \quad (4.9)$$

From Eq. (4.9), we can see that δe_{ij} and $\delta\epsilon_{\lambda\mu}$ transform each other as contravariant tensor. It is noteworthy that e_{ij}^L and e_{ij} transform to $e_{\lambda\mu}^A$ and $e_{\lambda\mu}^G$ respectively, whereas δe_{ij}^L and δe_{ij} transform to the same quantity $\delta\epsilon_{\lambda\mu}$ defined by Eq. (4.7)

§ 5. Derivation of Stress-Strain Relations

Let the Euler's and Lagrange's representation of stress be $T^{\lambda\mu}$ and σ^{ij} , respectively, then we have

$$T^{\lambda\mu} = 1/D x_{,\lambda}^{*i} x_{,\mu}^{*j} \sigma^{ij} \text{ or } \sigma^{ij} = D x_{,\lambda}^{*i} x_{,\mu}^{*j} T^{\lambda\mu} \quad (5.1)$$

where D is the volume magnification ratio. Let the Helmholtz free energy per unit volume before deformation be A , then we have, for isothermal process

$$\delta A = \sigma^{ij} \delta e_{ij}^L \text{ or } \sigma^{ij} = \frac{\partial A}{\partial e_{ij}^L} \quad (5.2)$$

If the material is isotropic in its initial state, we have

$$A = A(I_L, II_L, III_L) \quad (5.3)$$

where I_L , II_L and III_L are defined by Eq. (3.1). Then, from the second of Eq. (5.2) and Eq. (5.3), we can obtain

$$\sigma^{ij} = \frac{\partial A}{\partial I_L} \delta^{ij} + \frac{\partial A}{\partial II_L} e_{ij}^L + \frac{\partial A}{\partial III_L} e_{ik}^L e_{kj}^L \quad (5.4)$$

Substituting the second of Eq. (5.2) into the first of Eq. (5.1) and taking Eq. (3.13), Eq. (5.3) into account, we have Rivlin's equation as follows:⁴⁾

$$T^{\lambda\mu} = \frac{2}{D} \left\{ g'^{\lambda\mu} \frac{\partial A}{\partial I_L'} + (I_L' g'^{\lambda\mu} - g'^{\lambda\nu} g'^{\mu\nu}) \frac{\partial A}{\partial II_L'} + III_L' \delta_{\lambda\mu} \frac{\partial A}{\partial III_L'} \right\} \quad (5.5)$$

where I_L' , II_L' , III_L' are defined by Eq. (3.2).

Substituting Eq. (2.10) into Eq. (5.5), and using the relation $D=III_L'^{\frac{1}{2}}$ we have

$$T^{\lambda\mu} = \frac{2}{III_L'^{\frac{1}{2}}} \left\{ \left(\frac{\partial A}{\partial I_L'} - \frac{\partial A}{\partial II_L'} + I_L' \frac{\partial A}{\partial III_L'} \right. \right. \\ \left. \left. + III_L' \frac{\partial A}{\partial III_L'} \right) \delta_{\lambda\mu} + 2 \left(\frac{\partial A}{\partial I_L} - 2 \frac{\partial A}{\partial II_L'} \right. \right. \\ \left. \left. + I_L' \frac{\partial A}{\partial III_L'} \right) e_{\lambda\mu}^{\sigma} - 4 \frac{\partial A}{\partial III_L'} e_{\lambda\nu}^{\sigma} e_{\nu\mu}^{\sigma} \right\} \quad (5.6)$$

From Eq. (3.19), (3.20) and (3.22), we can see that I_L' , II_L' and III_L' are functions of I_G'' , II_G'' and III_G'' . Therefore, Eq. (5.6) can be rewritten as follows:

$$T^{\lambda\mu} = F_0 \delta_{\lambda\mu} + F_1 e_{\lambda\mu}^{\sigma} + F_2 e_{\lambda\nu}^{\sigma} e_{\nu\mu}^{\sigma} \quad (5.7)$$

where F_0 , F_1 and F_2 are functions of Green's strain invariants I_G'' , II_G'' , III_G'' . Eq. (5.7) is equivalent to Reiner's equation.

Let us apply the similar procedure above to e_{ij} and σ'^{ij} , where e_{ij} is defined by Eq. (2.9) and σ'^{ij} is defined by

$$T^{\lambda\mu} = \frac{1}{D} x_{,\lambda}^i x_{,\mu}^j \sigma'^{ij} \text{ or } \sigma'^{ij} = D x_{,\lambda}^* x_{,\mu}^* T^{\lambda\mu} \quad (5.8)$$

If we substitute the second equations of Eq. (5.1) and Eq. (4.8) into the first of Eq. (5.2), we have

$$\delta A = D T^{\lambda\mu} \delta \varepsilon_{\lambda\mu} \quad (5.9)$$

Then, substituting the first equations of Eq. (5.8) and Eq. (4.9) into Eq. (5.9), we have

$$\delta A = \sigma'^{ij} \delta e_{ij} \text{ or } \sigma'^{ij} = \frac{\partial A}{\partial e_{ij}} \quad (5.10)$$

which corresponds to Eq. (5.2).

From Eq. (3.13), Eq. (3.17) and Eq. (3.27), we can see that I_L , II_L , and III_L are functions of I , II , III which are defined by Eq. (3.7). Accordingly, if the material is isotropic in an undeformed state, we have

$$A = A(I, II, III) \quad (5.11)$$

as well as Eq. (5.3). Then, from the second of Eq. (5.10) and Eq. (5.11), we have

$$\sigma'^{ij} = \frac{\partial A}{\partial I} \delta_{ij} + \frac{\partial A}{\partial II} e_{ij} + \frac{\partial A}{\partial III} e_{ik} e_{kj} \quad (5.12)$$

which corresponds to Eq. (5.4).

Substituting the second of Eq. (5.10) into the first of Eq. (5.8) and taking Eq. (3.17), Eq. (5.11) into account, we can obtain

$$T^{\lambda\mu} = - \frac{2}{D} \left\{ g'_{\lambda\mu} \frac{\partial A}{\partial I} + (I' g'_{\lambda\mu} - g'_{\lambda\nu} g'_{\nu\mu}) \frac{\partial A}{\partial II'} \right. \\ \left. + III' \delta_{\lambda\mu} \frac{\partial A}{\partial III'} \right\} \quad (5.13)$$

which corresponds to Eq. (5.5). Substituting Eq. (2.8) into Eq. (5.13) and using the relation $D=III'^{-\frac{1}{2}}$, we have

$$T^{\lambda\mu} = -2III'^{\frac{1}{2}} \left\{ \left(\frac{\partial A}{\partial I'} - \frac{\partial A}{\partial II'} + I' \frac{\partial A}{\partial II'} \right. \right. \\ \left. \left. + III' \frac{\partial A}{\partial III'} \right) \delta_{\lambda\mu} - 2 \left(\frac{\partial A}{\partial I'} - 2 \frac{\partial A}{\partial II'} \right. \right. \\ \left. \left. + I' \frac{\partial A}{\partial III'} \right) e_{\lambda\mu}^A - 4 \frac{\partial A}{\partial III'} e_{\lambda\nu}^A e_{\nu\mu}^A \right\} \quad (5.14)$$

From Eq. (3.15), (3.16) and Eq. (3.25), we can see that I' , II' and III' are functions of I'_A , II'_A , and III'_A . So, Eq. (5.14) can be rewritten as follows:

$$T^{\lambda\mu} = G_0 \delta_{\lambda\mu} + G_1 e_{\lambda\mu}^A + G_2 e_{\lambda\nu}^A e_{\nu\mu}^A \quad (5.14)$$

Where G_0 , G_1 , and G_2 are functions of invariants of Almansi measure I'_A , II'_A and III'_A . Again, we have arrived at Reiner's equation.¹⁾⁵⁾

§ 6. Conclusion

It has been shown that

- i) σ'^{ij} and e_{ij} can play the role of σ^{ij} and e_{ij}^T , for our scheme to derive stress-strain relations. When the material is initially isotropic, stress-strain relation in terms of σ'^{ij} and e_{ij}^T results in Reiner's equation in terms of $T^{\lambda\mu}$ and $e_{\lambda\mu}^{\sigma}$, whereas if we start from stress-strain relation in terms of σ'^{ij} and e_{ij} , we arrive at Reiner's equation in terms of $T^{\lambda\mu}$ and $e_{\lambda\mu}^A$.
- ii) σ'^{ij} and $T^{\lambda\mu}$ transform with each other as contravariant tensor of weight 1, whereas σ'^{ij} and $T^{\lambda\mu}$ do as covariant tensor. σ'^{ij} seems to be rather an artificial quantity, but we must remember that σ^{ij} also was somewhat artificial one.

- iii) e_{ij}^T and $e_{\lambda\mu}^A$ transform with each other as covariant tensor, as it is well known, whereas e_{ij} and $e_{\lambda\mu}^{\sigma}$ do as contravariant tensor.

δe_{ij}^T transforms to $\delta \varepsilon_{\lambda\mu}$ as covariant tensor, whereas δe_{ij} transforms to $\delta \varepsilon_{\lambda\mu}$ as contravariant tensor.

- iv) Any one of the three sets which are defined, as above-mentioned, to a measure, determines definitely the other two belonging to the same measure.

The 1st, 2nd and 3rd invariant which constitute a set belonging to e_{ij}^T are equivalent to the 1st, 2nd and 3rd invariant of the corresponding set belonging to $e_{\lambda\mu}^{\sigma}$, respectively.

Such relations hold also between e_{ij} and $e_{\lambda\mu}^A$.

Each of I'_L , II'_L , and III'_L is a function of I' , II' , III' and each of I'_A , II'_A , and III'_A is of I'_G , II'_G , and III'_G .

References

- 1) For instance, M. Reiner: *Phenomenological Macrorheology, Rheology* vol. **1**, ed. by F. R. Eirich (Academic Press, New York, 1956) chap. 2.
- 2) M. Reiner and L. Rintel: The Bulletin of the Research Council of Israel, **6c** (1958) 113.
- 3) For instance, T. Alfrey: *Mechanical Behaviors of High Polymer* (Interscience. Publ. New York, 1948) 21.
- 4) W. Segawa: Reports on Progress in Polymer Physics in Japan (1959) 36. J. Phys. Soc. Japan **14** (1959) 1102.
- 5) M. Reiner: Amer. J. Math. **70** (1948) 43.
- 6) For instance, V. V. Novozhilov: *Foundation of the Nonlinear Theory of Elasticity* (Graylock Press, New York, 1953) 79, 145.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 15, No. 3, MARCH, 1960

On Similar Solutions of the Steady Quasi-two-dimensional Incompressible Laminar Boundary-layer Equations

By Nisiki HAYASI

Transportation Technical Research Institute, Mitaka, Tokyo

(Received November 5, 1959)

Using the orthogonal curvilinear coordinates, three-dimensional incompressible laminar boundary-layer equations are obtained. These equations reduce to two-dimensional type, if one component of the velocity and the pressure gradient in that direction are negligible throughout the boundary layer.

Conditions for the existence of similar solutions for such quasi-two-dimensional boundary layer are investigated. New similar solutions are found using "planar coordinates" α , β , γ ($\gamma=0$ gives the surface) in the case where the velocity at the outer edge of the boundary layer is expressed as $\{B_1 G(\alpha, \beta) + B_2\}^m$ or $B_2 \exp \{B_1 G(\alpha, \gamma)\}$, where m is a constant, B_1 and B_2 are arbitrary functions of β , and $G(\alpha, \beta)$ is a known function determined by the surface geometry

§ 1. Introduction

Since Prandtl¹⁾ proposed the boundary-layer theory, many exact solutions of the steady incompressible laminar boundary-layer equations have been obtained. Most of them are similar or affine solutions, for which one component of the velocity has the property that two velocity profiles located at different coordinates differ only by a scale factor. The first of such similar solutions was given by Blasius²⁾ for the flow past a flat plate. Subsequently the solutions for flows of the following types have been found: the flow near a stagnation point³⁾, the flow through a converging channel⁴⁾, and the flow past a wedge⁵⁾⁶⁾. These belong to the problems of

the two-dimensional flow. Mangler⁷⁾ and Hatanaka⁸⁾ have found independently a convenient transformation which reduces the axisymmetric problem to the equivalent two-dimensional problem. Using this transformation, Mangler⁷⁾ solved the problem for the flow due to a point sink on a flat plate or the flow due to a uniform line sink perpendicular to a flat plate. These are the examples which belong to the problems of the axisymmetric flows. Recently, Hansen⁹⁾¹⁰⁾ obtained similar solutions for three-dimensional boundary-layer flows for the case of developable surfaces and for the case of proportional main stream velocity components. However, his treatment cannot be applied to

the boundary-layer flows over an arbitrary surface, if one velocity-component of the main stream vanishes. In this paper, we try to obtain other kinds of similar solutions for three-dimensional boundary-layer flows.

§ 2. Boundary-layer Equations in Orthogonal Curvilinear Coordinates

The equations of continuity and of motion for incompressible flow, using a set of orthogonal curvilinear coordinates α, β, γ with scale factors A, B and C , are known⁽¹⁾. Let (u, v, w) and (X, Y, Z) be the components of the velocity and the external force in the directions of α, β, γ increasing, ρ the density, and p the pressure. Then, by the boundary-layer approximations $w \ll u$,

$$\frac{1}{C} \frac{\partial}{\partial \gamma} \gg \frac{1}{A} \frac{\partial}{\partial \alpha}, \frac{1}{B} \frac{\partial}{\partial \beta},$$

the non-dimensional equations of continuity and of motion reduce to

$$\frac{\partial}{\partial \alpha}(BCu) + \frac{\partial}{\partial \beta}(CAv) + \frac{\partial}{\partial \gamma}(ABw) = 0, \quad (1)$$

$$\begin{aligned} Du + \frac{wu}{CA} \frac{\partial A}{\partial \gamma} + \frac{v}{AB} \left(u \frac{\partial A}{\partial \beta} - v \frac{\partial B}{\partial \alpha} \right) \\ = X - \frac{1}{\rho A} \frac{\partial p}{\partial \alpha} + \frac{1}{BC} \frac{1}{Re} \frac{\partial}{\partial \gamma} \left(\frac{B}{CA} \frac{\partial Au}{\partial \gamma} \right), \end{aligned} \quad (2)$$

$$\begin{aligned} Dv - \frac{u}{AB} \left(u \frac{\partial A}{\partial \beta} - v \frac{\partial B}{\partial \alpha} \right) + \frac{vw}{BC} \frac{\partial B}{\partial \gamma} \\ = Y - \frac{1}{\rho B} \frac{\partial p}{\partial \beta} + \frac{1}{CA} \frac{1}{Re} \frac{\partial}{\partial \gamma} \left(\frac{A}{BC} \frac{\partial Bv}{\partial \gamma} \right), \end{aligned} \quad (3)$$

$$- \frac{v^2}{BC} \frac{\partial B}{\partial \gamma} - \frac{u^2}{CA} \frac{\partial A}{\partial \gamma} = Z - \frac{1}{\rho C} \frac{\partial p}{\partial \gamma}, \quad (4)$$

where

$$D = \frac{\partial}{\partial t} + \frac{u}{A} \frac{\partial}{\partial \alpha} + \frac{v}{B} \frac{\partial}{\partial \beta} + \frac{w}{C} \frac{\partial}{\partial \gamma},$$

and $Re = U_0 L / \nu$, U_0, L and ν being reference velocity, reference length and kinematic viscosity, respectively.

Let us assume that $v = 0$, that the flow is steady, and that the external force vanishes. Then Eqs. (1), (2), (3) and (4) reduce to

$$\frac{\partial}{\partial \alpha}(BCu) + \frac{\partial}{\partial \gamma}(ABw) = 0, \quad (5)$$

$$\begin{aligned} \frac{u}{A} \frac{\partial u}{\partial \alpha} + \frac{w}{C} \frac{\partial u}{\partial \gamma} + \frac{wu}{CA} \frac{\partial A}{\partial \gamma} \\ = - \frac{1}{\rho A} \frac{\partial p}{\partial \alpha} + \frac{1}{BC} \frac{1}{Re} \frac{\partial}{\partial \gamma} \left(\frac{B}{CA} \frac{\partial Au}{\partial \gamma} \right), \end{aligned} \quad (6)$$

$$\frac{u^2}{A} \frac{\partial A}{\partial \beta} = \frac{1}{\rho} \frac{\partial p}{\partial \beta}, \quad (7)$$

$$\frac{u^2}{A} \frac{\partial A}{\partial \gamma} = \frac{1}{\rho} \frac{\partial p}{\partial \gamma}. \quad (8)$$

Without loss of generality, we may take $C = 1$.

§ 3. Similarity Solutions

We shall further assume that $\partial A / \partial \gamma = \partial B / \partial \gamma = O(1)$. The physical meaning of this assumption is that the thickness of the boundary layer δ is far less than the radii of curvature of the body surface. Then, from (7) and (8), we can show that $\partial p / \partial \gamma = O(1)$ and $\partial A / \partial \beta = \partial p / \partial \beta = O(\delta)$. In fact, differentiating (7) with respect to γ , we have

$$\frac{1}{A} \frac{\partial A}{\partial \beta} \frac{\partial}{\partial \gamma} (u^2) = O(1)$$

and hence $\partial A / \partial \beta = O(\delta)$, since $\partial / \partial \gamma = O(\delta^{-1})$. The flow in which $v = 0$, $\partial p / \partial \gamma = \partial B / \partial \gamma = O(1)$ and $\partial p / \partial \beta = O(\delta)$ may be called 'quasi-two-dimensional'. Then Eqs. (5) and (6) reduce to

$$\frac{\partial Bu}{\partial \alpha} + AB \frac{\partial w}{\partial \gamma} = 0, \quad (9)$$

$$\frac{u}{A} \frac{\partial u}{\partial \alpha} + w \frac{\partial u}{\partial \gamma} = \frac{U}{A} \frac{\partial U}{\partial \alpha} + \frac{1}{Re} \frac{\partial^2 u}{\partial \gamma^2}, \quad (10)$$

where U is the velocity at the outer edge of the boundary layer. If the main flow outside the boundary layer is irrotational, $\partial U / \partial \alpha$ may be replaced by $dU/d\alpha$.

Let us consider the conditions under which the boundary-layer flow is similar. For this purpose, we assume $u = U(\alpha, \beta) f'(z)$, where $z = r \sqrt{Re/g(\alpha, \beta)}$ and dash denotes differentiation. Naturally g is considered to be proportional to the thickness of the boundary layer. The boundary conditions for f are

$$f(0) = f'(\infty) = 0; \quad f'(\infty) = 1.$$

Substituting these equations, together with the one derived by integrating (9) with respect to γ , into (10), we have

$$\begin{aligned} \frac{A}{g^2} f''' + \left(\frac{U}{g} \frac{\partial g}{\partial \alpha} + \frac{1}{B} \frac{\partial BU}{\partial \alpha} \right) f f'' \\ + \frac{\partial U}{\partial \alpha} (1 - f'^2) = 0. \end{aligned} \quad (11)$$

Hence we must have

$$\frac{\partial U}{\partial \alpha} = \frac{dA}{g^2}, \quad \frac{U}{g} \frac{\partial g}{\partial \alpha} + \frac{U}{B} \frac{\partial B}{\partial \alpha} = \frac{eA}{g^2}, \quad (12)$$

d and e being certain constants. Then Eq.

(11) is reduced to

$$f''' + (d+e)ff'' + d(1-f'^2) = 0. \quad (13)$$

This equation has been treated by Blasius²⁾, Mangler⁶⁾, and others.

If $\partial U/\partial \alpha = 0$, then

$$U = U(\beta) \quad (14)$$

and $d=0$. Since the second equation of (12) is reduced to

$$\frac{\partial g^2}{\partial \alpha} + \frac{\partial \ln B^2}{\partial \alpha} g^2 = \frac{2eA}{U},$$

we have, in this case,

$$g = \sqrt{B(\beta) + 2eG(\alpha, \beta)/U} B, \quad (15)$$

where $B(\beta)$ is an arbitrary function of β , and

$$G(\alpha, \beta) = \int AB^2 d\alpha. \quad (16)$$

If $\partial U/\partial \alpha \neq 0$, we have, from (12),

$$U^{2e/d} \frac{\partial U}{\partial \alpha} = B_1(\beta) AB^2,$$

where B_1 is an arbitrary function of β , being not zero. Then we have

$$U = \{B_1(\beta)G(\alpha, \beta) + B_2(\beta)\}^m/m^m \quad (17)$$

when $1/m = 1 + 2e/d \neq 0$, and

$$U = B_2(\beta) \exp \{B_1 G(\alpha, \beta)\} \quad (18)$$

when $1/m = 0$, where $B_2(\beta)$ is an arbitrary function of β . From the first equation of (12), we have

$$\begin{aligned} g &= \frac{1}{B} \sqrt{\frac{dm^{m-1}}{B_1 \{B_1 G(\alpha, \beta) + B_2\}^{m-1}}} \\ &= \sqrt{\left| \frac{d}{B_1} \right| \frac{|U|^{(1-m)/2m}}{B}} \end{aligned} \quad (19)$$

when $1/m \neq 0$, and

$$g = \frac{1}{B} \sqrt{\frac{d}{B_1 B_2 \exp \{B_1 G(\alpha, \beta)\}}} = \frac{\sqrt{dUB_1}}{B} \quad (20)$$

when $1/m = 0$.

If we suppose that the boundary layer begins at $\alpha = \alpha_0(\beta)$, then we have the condition that $g \rightarrow 0$ as $\alpha \rightarrow \alpha_0$. Hence, from (19), B_2 is determined as $B_2 = -B_1 G(\alpha_0, \beta)$, when (a) $m < 1$ and $B_0 \neq 0$, where suffix 0 denotes the value at $\alpha = \alpha_0$, or (b) $A = 1$, $m < 1/3$, $B_0 = 0$ and $(\partial B/\partial \alpha)_0 \neq 0$, or (c) $A = 1$, $m < 1/5$, $B_0 = (\partial B/\partial \alpha)_0 = 0$ and $(\partial^2 B/\partial \alpha^2)_0 \neq 0$, and so on. For example, let us consider the case (b). If $A = 1$, $B_0 = 0$ and $(\partial B/\partial \alpha)_0 \neq 0$, for $\alpha = \alpha_0$, we can put $B(\alpha, \beta) = (\partial B/\partial \alpha)_0 (\alpha - \alpha_0)$, so that we have

$$\begin{aligned} G(\alpha, \beta) - G(\alpha_0, \beta) &= \int_{\alpha_0}^{\alpha} B^2 d\alpha \\ &= (\partial B/\partial \alpha)_0^2 (\alpha - \alpha_0)^3/3. \end{aligned}$$

Therefore

$$\begin{aligned} \{G(\alpha, \beta) - G(\alpha_0, \beta)\}^{(1-m)/2}/B \\ = 3^{(m-1)/2} \left(\frac{\partial B}{\partial \alpha} \right)_0^{-m} (\alpha - \alpha_0)^{(1-3m)/2} \end{aligned}$$

and we can make $g \rightarrow 0$ as $\alpha \rightarrow \alpha_0$, if $m < 1/3$. In the same way, other cases can be demonstrated. Also, from (15), when $A = 1$, it is clear that B is determined as $B = -2eG(\alpha_0, \beta)/U$, because in this case m is 0 in the above discussion.

Eqs. (14), (17) and (18) give the velocity distributions of the main flow which make the boundary layer similar, whereas Eqs. (15), (19) and (20) give the variation of the thickness of the similar boundary layer. On the other hand, the velocity distribution in the boundary layer is the same as what was obtained by the above-mentioned researchers.

From $\partial A/\partial \beta = O(\delta)$, it can be shown that the β coordinate surfaces must be planes¹²⁾ (neglecting $O(\delta)$). Thus, steady 'quasi-two-dimensional' boundary-layer flow can exist only in the coordinate system in which at least one family of coordinate surfaces consists of planes perpendicular to the wall. We shall call such coordinate systems 'planar coordinate systems'. Corresponding to any planar coordinate system, whose plane coordinate surfaces contain all the streamlines in the boundary layer, when the velocity distribution of the main flow satisfies the above-mentioned relations, the solutions of (13) will give new similar solutions of the boundary-layer equations.

§ 4. Boundary Layer on a Flat Plate

In this section, we consider the case where the wall is a plane. Let us take the γ -axis perpendicular to the wall, so that α and β coordinate surfaces are families of cylindrical surfaces perpendicular to the wall. Then we have clearly $\partial A/\partial \gamma = \partial B/\partial \gamma = 0$. Therefore the boundary layer on a flat plate is quasi-two-dimensional, provided $v = 0$.

In search of a planar coordinate system, we consider a smooth curve K on the plane. The curves parallel to K and their normals constitute the projection of our planar coordinate system on the plane. If we take the

distance r along a normal as α , and the angle θ between a normal and an arbitrarily chosen straight line on the plane as β , then $ds^2 = dr^2 + \{r + R_0(\theta)\}^2 d\theta^2$, where R_0 denotes the radius of curvature of K . Thus $A=1$ and $B=r+R_0(\theta)$.

In the case $U=U(\theta)$, (15) is reduced to

$$g = [E(\theta)\{r+R_0(\theta)\} + F(\theta)\{r+R_0(\theta)\}^{-2}]^{1/2}, \quad (21)$$

where $E(\theta) = 2e/3U(\theta)$ and $F(\theta)$ is an arbitrary function of θ . If we suppose that the boundary layer begins at $r=r_0(\theta)$, then F is determined as $F = -E(r_0+R_0)^3$, so that

$$g = \sqrt{E(r-r_0)} \times \frac{\sqrt{(r+R_0)^2 + (r+R_0)(r_0+R_0) + (r_0+R_0)^2}}{r+R_0}. \quad (22)$$

For each stream surface $\theta = \text{const.}$, which is perpendicular to the wall, the variation of the boundary-layer thickness is of the same

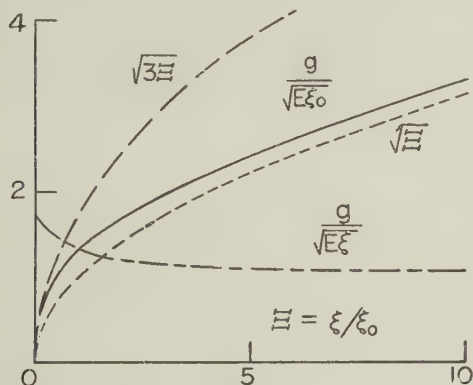


Fig. 1. (a)

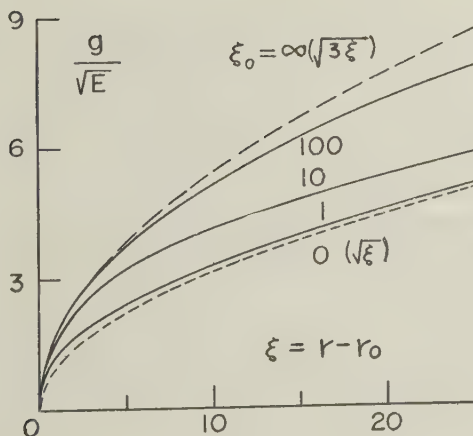


Fig. 1. (b)

Fig. 1. The variation of g as compared with the square-root law.

form, irrespective of the shape of the basic curve K . Indeed, (22) can be written as

$$g = \sqrt{E\xi} \frac{\sqrt{(\xi+\xi_0)^2 + (\xi+\xi_0)\xi_0 + \xi_0^2}}{\xi+\xi_0}$$

with $\xi = r - r_0(\theta)$, $\xi_0 = r_0(\theta) + R_0(\theta)$. Thus, for example, the boundary-layer thickness is exactly the same as that for the rotationally symmetric boundary layer on an infinite plane wall, having a circular hole of radius ξ_0 . This is shown in Fig. 1, where comparison is made with the square-root law in the

Blasius flow. When we can use Cartesian coordinates as the planar coordinates, as in the case of parallel flows, we have $R_0 = \infty$. Then, from (22), we have $g = \sqrt{3E\xi}$. On the other hand, when we can use cylindrical polar coordinates as the planar coordinates, as in the case of radial flows, we have $R_0 = 0$. If there is no hole on the wall, $r_0 = 0$. Then we have $g = \sqrt{E\xi}$. In the general quasi-two-dimensional flow as well as general rotationally symmetric flow with a hole, $g = \sqrt{3E\xi}$ in the region where $\xi \ll \xi_0$, whereas $g = \sqrt{E\xi}$ in the region where $\xi \gg \xi_0$. In other words, the variation of the boundary-layer thickness in quasi-two-dimensional flow is two-dimensional at the beginning, and is rotationally symmetric at the end. On the other hand, the velocity distribution in the boundary layer is the same as what was obtained by Blasius²⁾ and Tani¹³⁾.

It should be remarked here that, if the main flow is irrotational, U and E must be constants for the existence of similar flows.

If $\partial U / \partial r \neq 0$, (17) and (18) are reduced to $U = \{\Theta_1(r+R_0)^3 + \Theta_2\}^m$ when $1/m \neq 0$, and

$$U = \Theta_2 \exp \{\Theta_1(r+R_0)^3\}$$

when $1/m = 0$, where Θ_1 and Θ_2 are arbitrary functions of θ . From (19) and (20) we have

$$g = \sqrt{|d/3m\Theta_1|} |U|^{(1-m)/2m} (r+R_0)$$

when $1/m \neq 0$, and

$$g = \sqrt{|d/3U\Theta_1|} (r+R_0)$$

when $1/m = 0$. If we suppose that the boundary layer begins at $r=r_0(\theta)$, Θ_2 is determined as $-\Theta_1(r_0+R_0)^3$, when $m < 1$ and $r_0+R_0 \neq 0$ or $m < 1/3$.

If the main flow is irrotational, it can be readily shown that $B = r + R_0(\theta) = R_1(r)\Theta(\theta)$, where $R_1(r) = \sqrt{|dU/dr|} |U|^{e/a}$. Therefore, $R_0(\theta)$ must be a constant ($\Theta(\theta)$ being also constant), and so the curve K must be a

straight line or a circle. Then our planar coordinate system is reduced to Cartesian or cylindrical polar coordinate system.

§ 5. Boundary Layer on a Certain Kind of Surfaces

The arguments in the previous section can be extended to the more general case as follows. Let us consider a fixed plane M and a movable plane N (Fig. 2). On M is located a smooth curve K , while on N a straight line G and a smooth curve L are drawn.

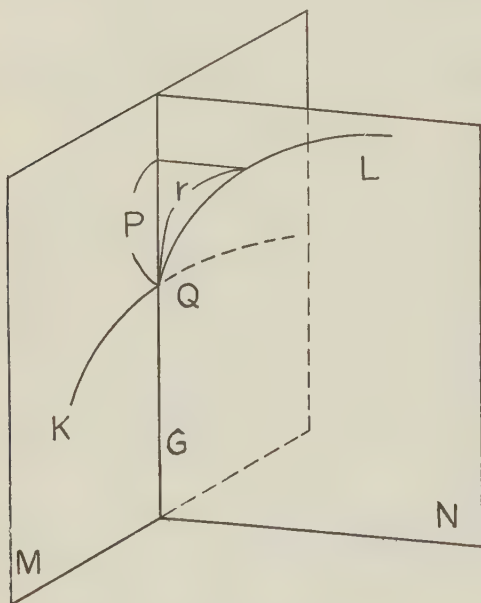


Fig. 2. A sketch of a certain surface.

Then suppose that N is moved in such a manner that G slides on M and L intersects with K , N being kept normal to K . L will make a surface S . We consider the boundary layer on S , assuming that the stream-line at the outer edge of the boundary layer is on N everywhere. We shall take as α the distance r from Q along L , Q being the point of intersection of K and L , and as β the angle of rotation θ of N from some fixed orientation. Further, we shall take the distance from S as r . It is evident that such a planar coordinate system is orthogonal, and that $A=1$ and $C=1$. B is given by $B=R_0(\theta)+P(r)$, where $P(r)$ is the projected distance (on M) of a point on L from Q .

Then the boundary-layer equations are reduced to (9) and (10). Therefore the arguments in the previous sections are also valid

in the present case except for B .

In the case $U=U(\theta)$, (15) is reduced to

$$g = \frac{\sqrt{3E(\theta)G(r, \theta) + F(\theta)}}{P(r) + R_0(\theta)}, \quad (23)$$

where

$$G(r, \theta) = R_0^2 r + 2R_0 \int_0^r P dr + \int_0^r P^2 dr.$$

If we suppose that the boundary layer begins at $r=r_0(\theta)$, then F is determined as $F = -3EG(r_0, \theta)$, so that

$$g = \sqrt{3E} \frac{\sqrt{G(r, \theta) - G(r_0, \theta)}}{P(r) + R_0(\theta)}. \quad (24)$$

If the main flow is irrotational, U and E must be constants for the existence of similar flows, as noted before.

In the case $\partial U / \partial r \neq 0$, (17) and (18) are reduced to

$$U = \{\Theta_1 G(r, \theta) + \Theta_2\}^m$$

when $1/m \neq 0$, and

$$U = \Theta_2 \exp \{\Theta_1 G(r, \theta)\}$$

when $1/m = 0$. From (19) and (20) we have

$$g = \sqrt{|d/m\Theta_1|} |U|^{(1-m)/2m} / (P + R_0)$$

when $1/m \neq 0$, and

$$g = \sqrt{d/U\Theta_1} / (P + R_0)$$

when $1/m = 0$. If we suppose that the boundary layer begins at $r=r_0(\theta)$, when the condition as given in § 3 is satisfied, $\Theta_2 = -\Theta_1 G(r_0, \theta)$.

If the main flow is irrotational, it can be readily shown that $B = P(r) + R_0(\theta) = R_1(r)\Theta(\theta)$. Then two cases arise.

(a) $P=0$, $R_1=\text{const}=k_1$, $R_0(\theta)=k_1\Theta(\theta)$. (The case $P=\text{const}$. can be easily reduced to that of $P=0$ by a simple modification of K .) $P=0$ means that L is a straight line perpendicular to the plane M . Thus the wall S is a cylindrical surface perpendicular to M . It may be interesting to note that Howarth¹⁴⁾ has pointed out that in such cases the boundary-layer equations may be taken in Cartesian form. Since Θ is an arbitrary function of θ , $R_0(\theta)$ is also an arbitrary function in this case. From $R_1=k_1$, it can be readily obtained that $U=(k_2 r + k_3)^m$ when $1/m \neq 0$ and $U=k_2 \exp(k_3 r)$ when $1/m = 0$, where k_2 and k_3 are constants.

(b) $R_0=\text{const}=k_1$, $\Theta=\text{const}=k_2$, $P=k_2 R_1 - k_1$. In this case, we are obviously concerned with the two-dimensional or axisym-

metric boundary layer.

After the completion of this paper, it was brought to the author's attention that Sedney¹⁵⁾ has already shown that there is no secondary flow in the boundary layer if the external flow streamlines are geodesics of the body surface. The boundary-layer flows treated in this paper belong to such category. Since, however, detailed discussions are not given in his paper, the author believes that it would be worthwhile to present his own result.

Acknowledgements

In conclusion, the author wishes to express his heartiest gratitude to Professor Isao Imai and Mr. Toshio Kawasaki for their kind discussions and valuable suggestions.

References

1) L. Prandtl: Verhandlg. d. III. Intern. Math. Kongr. (Heidelberg, 1904).
2) H. Blasius: Z. Math. Phys. **56** (1908) 1; also N. A. C. A. Tech. Memo. no. 1256.
3) K. Hiemenz: Göttinger Diss. 1911; also Dingler's Polytech. J. **326** (1911) 321.

4) K. Pohlhausen: Z. angew. Math. Mech. **1** (1921) 252.
5) D. R. Hartree: Proc. Cambr. Phil. Soc. **33** (1937) 223.
6) W. Mangler: Z. angew. Math. Mech. **23** (1943) 241.
7) W. Mangler: Z. angew. Math. Mech. **28** (1948) 97.
8) H. Hatanaka: Rep. Inst. Sci. Technol. Univ. Tokyo **3** (1949) 115.
9) A. G. Hansen: N. A. C. A. Tech. Memo. no. 1437 (1958).
10) P. L. Yohner and A. G. Hansen: N. A. C. A. Tech. Note no. 4370 (1958).
11) H. L. Dryden, F. D. Murnaghan and H. Bateman: *Hydrodynamics* (Nat. Res. Council, Nat. Acad. Sci. Washington, 1932); also Dover Publications, Inc. New York, 1956, p. 267.
12) P. M. Morse and H. Feshbach: *Methods of Theoretical Physics*, vol. **1** (McGraw-Hill Book Co., New York, 1953) 27.
13) I. Tani: J. Aero. Res. Inst. Tôkyô Imp. Univ. no. 245 (1945) 37.
14) L. Howarth: Phil. Mag. **42** (1951) 239.
15) R. Sedney: Q. Appl. Math. **15** (1957) 113.

Errata

A 160 cm Synchro- and Variable Energy Ordinary Cyclotron

By Seishi KIKUCHI et al.
J. Phys. Soc. Japan **15** (1960) 41

Page	Column	Line		Should be read
41	names of authors	4 in names	Keigo NISHIMURA	Keigo NISIMURA
		7 in names	Hiroshi OGAWA	Hirotsugu OGAWA
44	Table I	3	70 tons	270 tons
49	left	15 from bottom	plate 4 mm	plate 3 mm
	right	Fig. 8	G, H: Dee veltage	G, H: Dee voltage
50	left	10 from bottom	an aluminium plate	a copper plate
55	left	Fig. 16	$B_0=1.00$ Wb/m ²	$B_0=1.76$ Wb/m ²
			$B_0=1.76$ Wb/m ²	$B_0=1.00$ Wb/m ²
56	left	Fig. 17	B: Tuntable	B: Turntable

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm $\times$ 7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 528

Heat Capacity of a Single Crystal of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}^*$

By H. FORSTAT, G. O. TAYLOR and B. R. KING

*Department of Physics and Astronomy
Michigan State University, East
Lansing, Michigan, U. S. A.*

(Received January 6, 1960)

Friedberg and Wasscher¹⁾ have measured the heat capacity of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ by using approximately 88 gm of the salt which consisted of a great number of small crystals. This is equivalent to making a powder measurement except that a size effect correction was not necessary since the crystals were about 3 mm in average dimension. They reported observing an antiferromagnetic-paramagnetic transition at the Néel temperature of 1.622°K.

During the course of some work on the magnetic properties of single crystals of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ it was felt desirable to perform a heat capacity measurement on a single crystal, so that there might not be any question in comparing the magnetic experiments with heat capacity data. In this connection it should be noted that the work on the magnetic susceptibility and relaxation processes^{2),3)} included experiments on both a single crystal and a powder sample because it was felt that the poor thermal conductivity might affect the relaxation mechanism.

In the present experiment, the heat capacity measurements were carried out in a calorimeter used previously for work on azurite⁴⁾, $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ ⁵⁾ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ ⁶⁾. The single crystal of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was grown from an aqueous solution at room temperature and weighed 2.58 gm. It was approximately $2 \times 1.5 \times 1.0$ cm in size. Heat capacity data

were taken in the temperature range 1.17–4.43°K using a 1/10 watt, 56 ohms Allen-Bradley resistor as a thermometer. The results of the measurements are shown in Fig. 1.

A λ -type anomaly, characteristic of a phase transition ordering process, was observed at $1.60 \pm 0.01^\circ\text{K}$. This transition has been identified as an antiferromagnetic-paramagnetic one by the work on the magnetic susceptibility^{2),3)} and the proton resonance⁷⁾. Within the experimental error, this Néel temperature agrees with the heat capacity work of Friedberg and Wasscher¹⁾, indicating that they were able to achieve fairly good thermal equilibrium with their use of helium exchange gas.

An estimate has been made of the magnetic entropy change which occurs as the crystal cools through the transition temperature. This same calculation has been used in the case of other crystals^{4),5),6)} and consists of determining the contributions to the magnetic entropy in the paramagnetic state (the characteristic tail in the heat capacity curve) and separately, in the antiferromagnetic state. By assuming that the heat capacity is inversely proportional to the square of the temperature in the paramagnetic state and correcting for the lattice specific heat, a value of 0.20 cal/mole-deg is obtained. In the antiferromagnetic state a graphical method is used to determine the area under the c_p/T vs T curve. This yields 3.30 cal/mole-deg. Therefore the total entropy change is 3.50 cal/mole-deg. Since the entropy change is given by $R \ln(2S+1)$ where $S=5/2$ for the ground state spin of Mn^{++} , this gives 3.55 cal/mole-deg. This seems to be a fair agreement.

It is of interest to observe that approximately 6% of the total entropy is gained above the Néel temperature, due probably to short range ordering effects.

References

- 1) S. A. Friedberg and J. D. Wasscher: *Physica* **19** (1953) 1072.
- 2) M. A. Lasheen, J. Van der Brock and C. J. Gorter: *Physica* **24** (1958) 1061.
- 3) M. A. Lasheen, J. Van der Brock and C. J. Gorter: *Physica* **24** (1958) 1076.
- 4) H. Forstat, G. O. Taylor and B. R. King: *J. Chem. Phys.* **31** (1959) 929.
- 5) R. D. Spence, H. Forstat, G. O. Taylor and G. A. Khan: *J. Chem. Phys.* **31** (1959) 555.
- 6) H. Forstat, G. O. Taylor and R. D. Spence: *Phys. Rev.* (to be published in November 1959).
- 7) R. D. Spence: private communication.

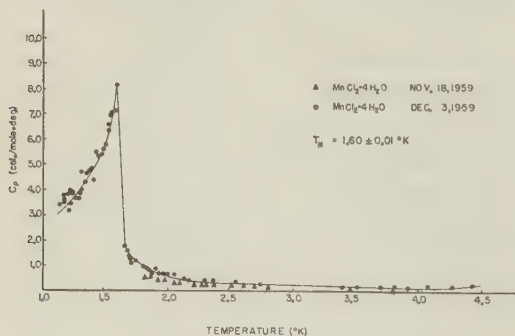


Fig. 1.

* Supported by the Office of Ordnance Research, U. S. Army.

J. PHYS. SOC. JAPAN **15** (1960) 529~530

Purification of Alkali Halide Crystals through Fractional Distillation and Normal Freezing

By Hiroshi KANZAKI and Keishiro KIDO

*The Institute for Solid State Physics,
The University of Tokyo*

(Received January 13, 1960)

During experimental studies for preparation of alkali halide crystals with the highest purity, we have found the following procedures are very useful for the purpose.

Firstly, the purity can be considerably improved by fractional distillation in a transparent quartz tube under high vacuum (10^{-6} mm Hg with liquid nitrogen trap). The first fraction is collected in a receiver nearest the trap and the middle fraction is collected in the next section. The concentration of multivalent cations in the middle fraction is always about one tenth of that in the starting material. The residue always contains higher concentration of cationic impurities than the middle fraction. Distillation procedure is also effective for removing anionic impurities. For example, crystals produced from the middle part are entirely free from extra optical absorption bands originating from oxide or hydroxide.

Secondly, single crystal has been grown by using the Bridgman, or normal freezing, method. The middle fraction described above is sealed off in quartz tube under high vacuum immediately after distillation and its melt is solidified by lowering the sealed quartz ampoule very slowly (2 mm per hour) along vertical temperature gradient. Under this condition of growth, any sign of reaction has never been observed between molten alkali halide and quartz tube, and crystals thus produced do not stick to quartz wall upon cooling to room temperature.

Seven crystals of KCl have been produced by using these procedures and three of them were long enough to study the segregation of impurities in the course of normal freezing process. In the following, experimental results on low temperature ionic conductivity will be described on one of the long crystals in order to show the effectiveness of removing multivalent cationic impurities by these procedures.

Starting material of the following experiments is Wako reagent grade potassium chloride. The KCl-F crystal in Fig. 1 was grown from original KCl powder without distillation. Its conductivity is a measure of concentration of multivalent cationic impurities in the starting material.

Several specimens were cleaved from each of grown crystals and their d.c. conductivity were

measured as a function of temperature. In Fig. 1, data are shown for three specimens from KCl-I crystal which was 65 mm long and 10 mm in diameter. Conductivity data of KCl-I-(1), (2) and (3) show the distribution of multivalent cationic impurities along the KCl-I crystal. The location of these specimens along KCl-I can be described by their value of "fraction g previously solidified" using Pfann's notation¹⁾. Values of g for (1), (2) and (3) are 0.02, 0.70 and 0.98, respectively. The results in Fig. 1 show clearly that cationic impurities effective for low temperature ionic conductivity are segregated with distribution coefficient less than unity. These data have been used to calculate the conductivity corresponding to average concentration of impurities in the crystal. Black circles in Fig. 1 show the results calculated for KCl-I crystal.

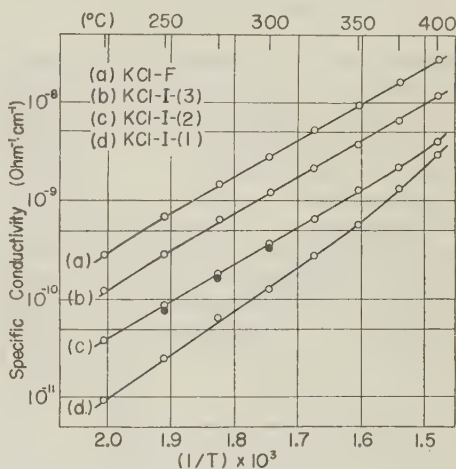


Fig. 1. Specific conductivity of KCl specimens against $1/T$.

We can estimate the effective concentration of divalent cationic impurities by using the value of vacancy mobility extrapolated from data by Kelting and Witt²⁾. The estimated values for these specimens are as follows:

Specimen	Concentration per cm^3 .
KCl-F	5.1×10^{16}
KCl-I-(1)	2.2×10^{15}
KCl-I-(2)	6.5×10^{15}
KCl-I-(3)	2.3×10^{16}
KCl-I average	6.2×10^{15}

It may be worth mentioning that effective distribution coefficient of multivalent cations is estimated to be about 0.4 in the case of KCl-I crystal.

It is a pleasure to record the value of cooperation with Dr. T. Ninomiya during this study. This work is partly supported by the Research Grant from the Ministry of Education.

References

- 1) W. G. Pfann: *Zone Melting* (John Wiley and Sons, New York, 1958) 10.
- 2) H. Kelting and H. Witt: *Z. Phys.* **126** (1949) 697.

J. PHYS. SOC. JAPAN **15** (1960) 530

Ferrimagnetic Resonance in Polycrystalline Europium-Iron Garnet ($\text{Eu}_3\text{Fe}_5\text{O}_{12}$)

By Yüzō SHICHIJŌ, Tomonao MIYADAI
and Hisao TAKATA

*Electrical Communication Laboratory, Nippon
Telegraph and Telephone Public Corporation,
Tokyo, Japan*

(Received December 10, 1959)

Although many and detailed investigations have been made on yttrium-iron garnet, detailed studies on the other garnets have not yet been done for the ferrimagnetic resonance. Here, we shall take up europium-iron garnet (EuIG) for which no data has been reported.

The specimens used were prepared by coprecipitation method from Eu_2O_3 (99.9% pure) and electrolytic iron metal. The heat-treatments were presintering of $1000^\circ\text{C} \times 2$ hrs, final sintering of

$1330^\circ\text{C} \times 5.3$ hrs (both in air) and cooling in the furnace. The specific gravity is 5.6 (relative density is 90%). Several spheres from 0.25 to 0.54 mm in diameter were polished for resonance experiment. The experimental errors in g -factor and line width are about 2 and 10%, respectively. The resonance absorption experiment was made at 18320 Mc by a usual microwave technique in the temperature range from -196°C to 300°C .

In Fig. 1 is shown the temperature-variation of the absorption curve. It is seen that a secondary peak appears near -90°C and that it becomes more intense at the cost of the old "main" peak as the temperature decreases.

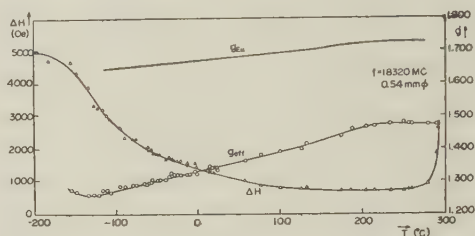


Fig. 2. Line width (ΔH), effective g -factor (g_{eff}) and calculated g -factor for $\text{Eu}^{3+}(g_{\text{Eu}})$ vs temperature.

ΔH and g_{eff} are shown in Fig. 2 as functions of temperature. g_{eff} 's at low temperatures are determined referring to the main peak. Although the line width seems to show a rather rapid increase at lower temperatures, it is expected that the line width associated with the main peak varies scarcely with temperature; actually, according to a preliminary experiment on a single crystal of EuIG, the line width at -196°C is about equal to that at room temperature. A minimum in ΔH occurs slightly below the Curie point. g_{eff} is as small as 1.34 at room temperature and has a slight linear dependence on temperature. We calculated the g -factor for Eu^{3+} , g_{Eu} by applying Tsuya-Wangsness formula¹⁾ for g_{eff} of ferrimagnetics with two magnetic sublattices under some assumptions. g_{Eu} obtained is also shown in Fig. 2 and seems to have a slight temperature dependence.

The secondary peak which appears at lower temperatures, could be explained following to Schlömann²⁾; at these temperatures the condition $M_s \ll H_a$ (M_s =saturation magnetization, H_a =effective anisotropy field), will be satisfied, resulting in appearance of a secondary peak.

The authors wish to express their thanks to Mr. T. Satō in the Laboratory for sample preparation.

References

- 1) N. Tsuya: *Progr. Theor. Phys.* **7** (1952) 263.
- R. K. Wangsness: *Phys. Rev.* **91** (1953) 1085.
- 2) E. Schlömann: *J. phys. radium* **20** (1959) 327.

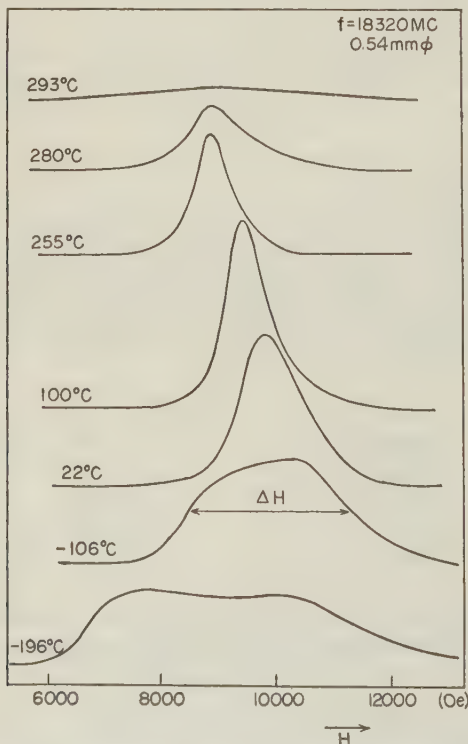


Fig. 1. Absorption curves at various temperatures.

J. PHYS. SOC. JAPAN 15 (1960) 531~532

Maser Oscillation on 6-6 Line of N¹⁵H₃*

By Isao TAKAHASHI, Tsuneo HASHI,
Masaru YAMANO, Motokazu YAMAMOTO,
Shigeyoshi SUZUKI

Department of Physics
and Tsutomu MAKITA

Department of Chemistry,
Faculty of Science, Kyoto University
(Received December 15, 1959)

The oscillation frequency of the maser on N¹⁴H₃ 3-3 line changes fairly with the focuser voltage and the source pressure^{1),2)}, mainly because of the hyperfine structure due to the electric quadrupole moment of N¹⁴ nucleus. This change may be absent in the case of N¹⁶H₃, since N¹⁶ has no electric quadrupole moment. We observed the characteristics of the maser on N¹⁶H₃ 6-6 line (23,922 Mc³) and referred to as *A*) and compared with those on N¹⁴H₃ 3-3 line (23,870 Mc³) and referred to as *B*), using the same maser device.

The samples used were N¹⁶H₃ prepared from ammonium sulphate 68% enriched in N¹⁶ (referred to as α) and natural ammonia (referred to as β).

The focuser consisted of eight cylindrical electrodes 355 mm long. The cavity was a cylindrical TM₀₁₀ mode cavity 100 mm long and had value of *Q* near 6,000. The superheterodyne detection system with 25 Mc intermediate frequency was used.

To estimate the intensity ratio *I_A/I_B* of the masers on *A* and *B*, we computed the quantity:

$$I = (\text{fractional population}^{4),5)}) \times (\text{efficiency of focusing}^{6)}) \times (\text{transition probability}^{6)}),$$

omitting other factors not serious in the present case. The obtained value of *I_A/I_B* was about 1.

Figs. 1 and 2 show the oscillation characteristics.

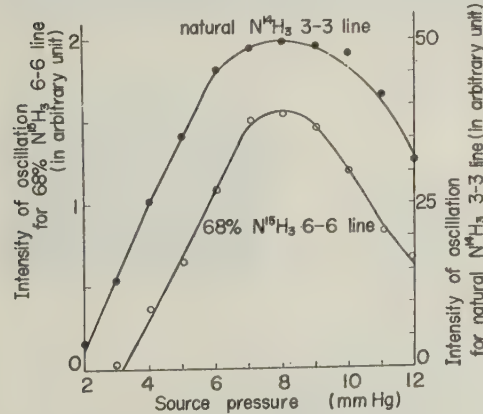


Fig. 1. Source pressure at the focuser voltage of 11.0 kV.

* Read before the meeting of the research group on the atomic frequency standard, Nov. 26, 1959.

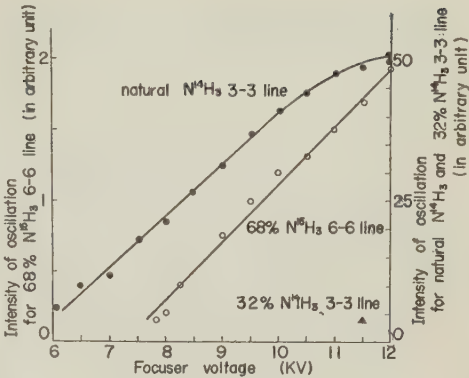


Fig. 2. Intensity of oscillation versus focuser voltage at the source pressure of 7 mm Hg.

Table I. Intensity ratio *I_A/I_B*.

value	0.3	0.05	0.04
from	threshold voltage	Fig. 1	Fig. 2

Here the values are referred to *B* in β at the same population by multiplying with the abundance ratio.

The threshold voltages for *A* in α and *B* in β had their minimum values 7.6 and 3.4 kV at the source pressure of 7 mmHg. The general features of the oscillation characteristics for *A* in α and *B* in β are alike. The multiplication of the intensity ratio of *B* in α and *B* in β by the abundance ratio 99/32 gives about 1/5. Thus the intensity of *B* in α seems to be considerably smaller than that of *B* in β at the same population of N¹⁴H₃. It is partly due to the effect of N¹⁶H₃. The effect of N¹⁴H₃ on the intensity of *A* in α may also be present.

Table I shows the intensity ratios evaluated from the observation. They differ from one another and also are so far from the theoretical value 1 that they cannot be compensated with the factor, say 5 (derived above). Further studies on the mutual influence between N¹⁴H₃ and N¹⁶H₃ are necessary.

The precise measurements on the shift of the oscillation frequency are now in progress.

The authors' thanks are due to Prof. N. Sasaki for his guidance in preparing the sample.

References

1) J. C. Helmer: J. Appl. Phys. **28** (1957) 212.
2) K. Shimoda: J. Phys. Soc. Japan **13** (1958) 939.
3) P. Kisliuk and C. H. Townes: *Molecular Microwave Spectra Tables*, (National Bureau of Standards. Circular 518, 1952).
4) G. Placzek and E. Teller: Z. Phys. **81** (1933) 209.
5) C. H. Townes and A. L. Shawlow: *Microwave Spectroscopy* (McGraw-Hill, New York, 1955) §§ 3~5.

- 6) J. P. Gordon, H. J. Zeiger and C. H. Townes:
Phys. Rev. **99** (1955) 1264.

J. PHYS. SOC. JAPAN **15** (1960) 532

Microwave Discharge Chamber

By Shūji FUKUI and Satio HAYAKAWA
*Physical Institute, Faculty of Science,
Nagoya University Nagoya, Japan*

(Received January 14, 1960)

Recently Fukui and Miyamoto¹⁾ have developed the discharge chamber as a detector of ionizing particles. In this short note we would like to propose the microwave discharge chamber that will result from the natural extension of our discharge chamber operated by D. C. pulses.

In spite of its merits in many respects, the D. C. discharge chamber has disadvantage in obtaining only a particle trajectory projected on a two-dimensional plane. The microwave discharge chamber seems to be get rid of this disadvantage in such a way that a pulsed intense alternating electric field of a high frequency is responsible not only for the multiplication of electrons produced by a particle to be detected but also for the effect of preventing the electrons and ions thus formed from drifting away from a region in which primary electrons are produced. In this way we shall be able to obtain such particle tracks that one is observing with cloud and bubble chambers.

In comparison with existing devices the advantage of the microwave discharge chamber may be seen in the following points. (I) The distortion of a track should be much less than that in the expansion chambers, the expansion inevitably giving rise to turbulent motions in the chambers. (II) The sensitive time is so short that the coincidence with other electronic devices is possible. (III) The construction is easy and the cost is rather small. The above points are expected from our experiences in the D. C. discharge chamber.

The working conditions of the microwave discharge chamber was investigated by reference to the theory and the experiment of the high frequency discharge^{2),3)}. Only essential points of them will be presented in what follows.

The analogy to the D. C. discharge is found if the effective strength of and alternating electric field, E_c , is used in place of a D. C. field of strength, E_d , which are connected by

$$E_c^2 = \frac{1}{2} \frac{\omega_m^2}{\omega^2 - \omega_m^2} E_d^2,$$

where ω is the angular frequency of the applied microwave and ω_m the frequency of collision for

momentum transfer. In order to obtain the width of a track of 1 mm, the drift length of electrons accelerated by a h.f. field is restricted also to be smaller than 1 mm, so that the value of E_c is related to the value of ω . If we use a conventional magnetron with $\omega/2\pi = 3000$ Mc/s and a mixture of Ne+0.5% A of atmospheric pressure, we may choose E_c as high as a few kV/cm on account of our previous experiences with the D. C. chamber as well as of $\omega^2 \ll \omega_m^2$ *. A pulsed microwave of this field strength should be applied no later than a few microseconds after a particle passed through the chamber, so that the primary electrons may not diffuse away. The duration of the pulse should be as short as 10^{-7} sec, equal to the duration of the D. C. pulse used for the D. C. chamber, so that the width of a track is as small as 1 mm and the background luminescences produced by photoelectrons are restrained. The number of excited atoms enough to give one a visible track must be produced by means of electronic collisions. The multiplication of electrons in a h.f. field is affected by the space charge produced. The field strength required above, therefore, corresponds to a rather high power of microwaves, several megawatts. In practice, however, we need not use a high power source but we may use a cavity of a reasonable Q value as the discharge chamber, so that a conventional magnetron is powerful enough for our purpose.

Finally a few remarks are mentioned. A magnetic field can be applied for measuring the rigidity of a particle. The magnetic field helps in sharpening the track, because it prevents electrons from drifting across the field. The light emitted from the excited gas of Ne+A is of short wave lengths. The use of a wave length shifter, such as quaterphenyl, increases the visibility of a track⁴⁾. Xenon is considered to be suitable for high energy physics, because of its high atomic number and of better visibility of its light emission. Details of the working conditions will be determined by experimental studies.

References

- 1) S. Fukui and S. Miyamoto: *Nuovo Cimento* **11** (1959) 113.
- 2) V. E. Golant: *UFN, USSR*, **65** (1958) 39.
- 3) S. C. Brown: *Basic Data of Plasma Physics* (The Technology Press, John Wiley and Sons, Inc. 1959).
- 4) A. Sayers and C. S. Wu: *Rev. Sci. Instr.* **28** (1957) 758.

* The breakdown voltage for this case is estimated to be about several hundreds of V/cm. The field strength of a few kV/cm is required for the multiplication of electrons enough to give a visible track.

J. PHYS. SOC. JAPAN **15** (1960) 533~534**Domain Patterns on Thin Films of Perminvar**By Yuzi GOMI, Yuzo ODANI
and Makoto SUGIHARA*Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation 1551,
Kichijoji, Musashino-shi
Tokyo, Japan*

(Received September 10, 1959)

Magnetic domain patterns in thin films were already observed on many magnetic materials by several investigators¹⁾. We have observed new interesting domain patterns in the films of the thickness range 300 Å to 2000 Å by the well-known Bitter technique. These patterns are thought to be important in investigating a crystal structure of thin films.

The films used in this work were made by evaporating perminvar (Fe30%, Co25%, Ni45%) on microscopic slides without magnetic field at a pressure of 1.10^{-5} mm Hg. The disturbance field of a filament current was below 0.02 oe. When a specimen has been demagnetized by an ac field, the domain pattern formed varies greatly with the direction of the ac demagnetizing field. It will show the presence of an uniaxial anisotropy along certain direction. That is, with the demagnetization by the ac field applied along the specific direc-

tion which is thought to coincide with that of the uniaxial anisotropy, the domains formed are largest in size and orientate themselves into this direction (Fig. 1(a)). As the direction of the ac demagnetizing field has been inclined from this preferred one, the domains become narrower.

When a dc magnetic field of over about 30 oe (nearly equal to the coercive force of this film) is applied along the preferred direction after ac demagnetization along the same direction, the domains with the same sense as the dc field become larger as has been expected. If, however, the dc field is applied at an angle of about $30^\circ \sim 60^\circ$ to the preferred direction, complicated patterns appear. That is, with increasing field strength over about 30 oe, the slender lines making 30° angle to the preferred direction appear in the domains which have the magnetization in opposite sense to the dc field, (Fig. 1(b)). The domain boundaries in Fig. 1(a) remain unchanged. If the field is decreased to zero and then increased along the opposite direction, the slender lines begin to appear in the domains where there were no slender lines before, and after the further increase of the field those lines cover the whole surface (Fig. 1(c)). If the dc field is applied perpendicular to the preferred direction, the contrast of the adjacent domains increases with increasing field as shown in Fig. 2(a). As soon as the field strength has reached to 30 oe, the domain pattern becomes abruptly complicated as shown in Fig. 2(b), and disappears instantaneously with increasing the dc field further.

The phenomena mentioned above is observed in the films evaporated without magnetic field on unheated substrates, and especially remarkable in the region produced by the oblique incidence of metal depositing beam, but not observed in those evaporated in the presence of magnetic field on the same conditions. If the evaporation was made on

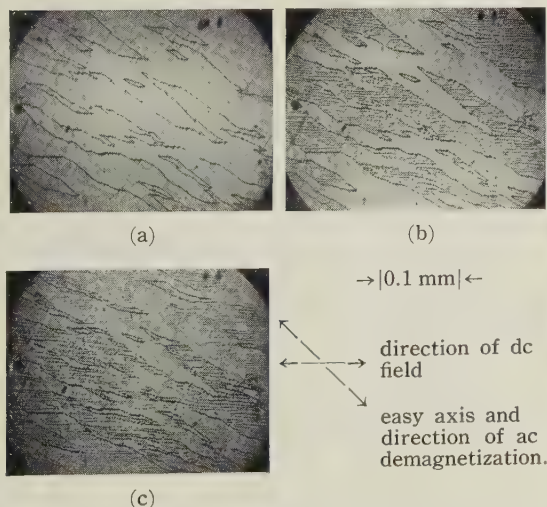


Fig. 1. Domain patterns observed in 450 Å Fe-Ni-Co film: (a) domain configuration after ac demagnetized along the direction of easy magnetization, (b) slender lines which appeared by applying the dc field just below H_c along the 30° from the easy axis, (c) slender lines covered whole surface by reversing the dc field in (b).

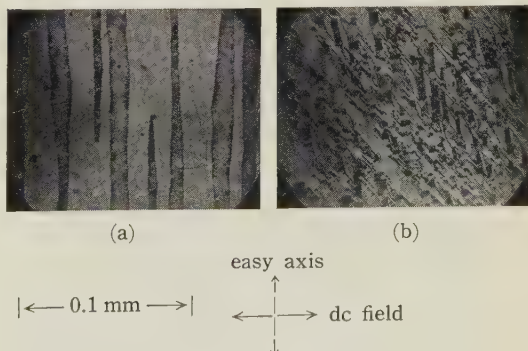


Fig. 2. Domain patterns with the dc field perpendicular to the easy axis in the film plane: (a) when applying the dc field less than H_c , (b) the complicated domains which appeared with a sudden break by increasing the dc field further in (a).

heated substrates, then the considerable winding of the slender lines appears. Similar phenomena is observed in the Co and the Fe films. Detailed results shall be reported later.

Reference

- 1) H. J. Williams and R. C. Sherwood: *J. Appl. Phys.* **28** (1957) 548. C. A. Fowler, Jr. and E. M. Fryer: *Phy. Rev.* **104** (1956) 552. H. W. Fuller and H. Rubinstein: *J. Appl. Phys. Suppl.* to **30** (1959) 84S etc.

J. PHYS. SOC. JAPAN **15** (1960) 534

Jump Phenomenon in Resonance Curve of Ferroelectric Ceramics

By Katsuo NEGISHI

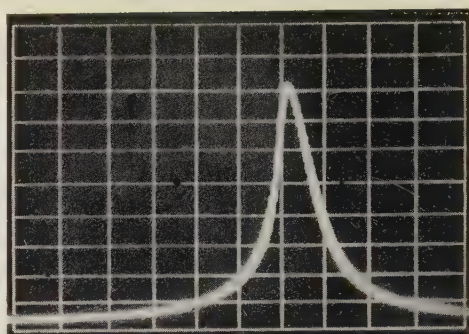
*Kobayasi Institute of Physical Research,
Kokubunji, Tokyo*

(Received December 17, 1959)

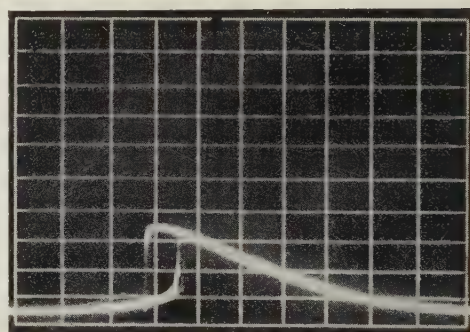
In the process of measuring the amplitude dependence of the mechanical Q of the ferroelectric ceramics, a jump phenomenon of the resonance curve was observed.

Fig. 1 shows the mechanical resonance curves of a circular disc of lead zirconate-titanate ceramics, 26.2 mm in diameter and 2.1 mm in thickness and resonating in a radial mode at 93.18 kc/s. The vertical axes are proportional to the motional admittance, and the top of the axes corresponds to about 25 mΩ. The horizontal or frequency axes are swept bidirectionally, one division corresponding to 100 c/s.

In Fig. 1 (a), the applied voltage is 0.1 V, and the resonance curve seems to be the same as that of a linear system. The mechanical Q is estimated at about 1700. By applying a driving voltage of 1 V, the peak of the resonance curve becomes inclined to the lower side of the frequency axis as in Fig. 1 (b). Fig. 1 (c) is the curve at 10 V showing the jump or hysteresis phenomenon. Compared



(b)



(c)

Fig. 1. Resonance curves of $\text{Pb}(\text{Zr-Ti})\text{O}_3$ ceramic resonator at various driving voltages.

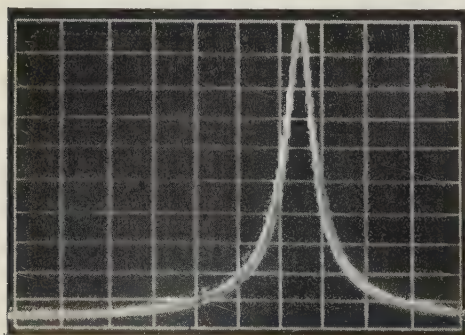
(a) 0.1 V. (b) 1 V. (c) 10 V.

with Fig. 1 (a), the peak of the curve shifts to lower frequency side by about 350 c/s and is reduced in height to one third.

These phenomena are explained by the nonlinear stiffness and damping of the resonator¹⁾. The strain amplitude of the resonator, at which the effect of the nonlinearity becomes to be noticed, is of the order of 10^{-6} . The nonlinear behavior was found in all of the tested ceramic specimens of lead zirconate-titanate system and barium titanate system, but the jump phenomenon did not occur except in the specimens of high mechanical, Q .

Reference

- 1) J. J. Stoker: *Nonlinear Vibration* (Interscience Pub. Inc., N. Y. 1950) 90.



(a)

J. PHYS. SOC. JAPAN **15** (1960) 535**Chain Wall in Permalloy Thin Films**

By YUZI GOMI and YUZO ODANI

Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, 1551, Kichijoji Musashino-shi, Tokyo, Japan

(Received January 11, 1960)

In permalloy thin films, Goodenough et al.¹⁾ have shown the existence of chain wall (shown in Fig. 1) as well as the well-known cross-tie wall²⁾. There must be the special origin for chain wall to exist, because only cross-tie walls are generally observed under usual conditions. Goodenough et al, nevertheless, did not show this origin. We have already observed also the similar walls and their modified types. Here, we shall report on these modified types and explain their origin.

The films used in this investigation were made by evaporating 80-20 permalloy on microscopic slides. During evaporation, a pressure of $1 \cdot 10^{-6}$ mmHg was maintained. Magnetic domain patterns were observed by the well-known Bitter figure technique.

The walls observed were almost cross-tie walls, and scarcely chain walls. In addition to walls mentioned above, in our work, the displaced types

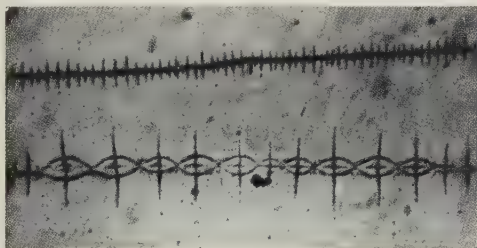
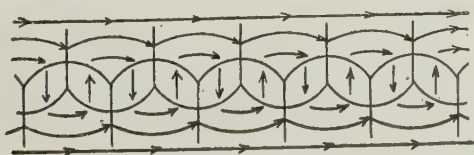


Fig. 1. Cross-tie wall and chain wall in permalloy films of 500 Å thickness.

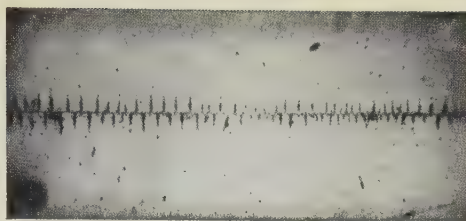


(a)

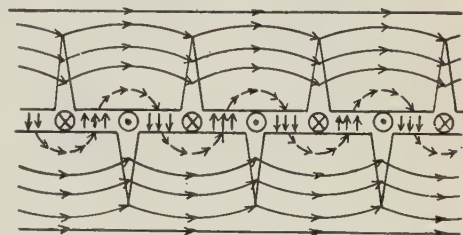


(b)

Fig. 2. (a) displaced chain wall and (b) its magnetic structure.



(a)



(b)

⊙ $\vec{M}$ vertically out of plane

⊗ $\vec{M}$ vertically into plane

Fig. 3. (a) displaced cross-tie wall and (b) its magnetic structure.

of these walls were observed also as shown in Figs. 2(a) and Fig. 3 (a). The magnetic structures of the displaced walls newly observed are supposed to take the distribution of the magnetization vectors as shown in Figs. 2 (b) and 3 (b).

Figs. 2 (b) and 3 (b) show that the magnetization vectors on the both sides of the displaced walls have the same sense. This means that these walls are originated by scratches or anisotropic inner stress, because they exist in a single domain. If the vectors of both sides are antiparallel, the walls around the scratches become usual type chain wall or cross-tie wall. Whether the walls formed are chain walls or cross-tie walls seems to be determined by the degree of magnitude of the scratch or anisotropic inner stress. Precisely speaking, if there is no scratch, there appear cross-tie walls only. If the scratch or inner stress is comparatively small, cross-tie wall or its displaced type appears. For the larger scratch or inner stress, chain wall or its displaced type appears, because in the neighborhood of the wall the anisotropic inner stress induced by the scratch makes the direction of easy axis of magnetization perpendicular to wall line with the action of magnetostriction. The behavior of the walls by applying dc magnetic field is now under investigation and it will be reported in near future.

References

- 1) J. B. Goodenough: J. phys. radium **20** (1959) 318 (Discussions).
- 2) E. E. Huber, Jr., D. O. Smith and J. B. Goodenough: J. Appl. Phys. **29** (1958) 284.

J. PHYS. SOC. JAPAN **15** (1959) 536~537**Diffuse Scattering of X-rays by Gamma-irradiated Rochelle Salt**By Koichi TOYODA, Akira SHIMADA*
and Tetsuro TANAKA*Institute for Chemical Research,
Kyoto University, Kyoto*

(Received January 23, 1960)

It has been reported by two of the present authors¹⁾ and Iurin²⁾ that peculiar changes occur in the ferroelectric and piezoelectric properties of Rochelle salt, when the crystals are subjected to γ -ray irradiations. It is noteworthy that with an increase of dosage, the ferroelectric region becomes narrow and the dielectric constant decreases, and with a further increase of dosage two Curie points essentially disappear; the electromechanical coupling factor is affected in the same way as the case of dielectric constant. Peculiar changes appeared in the ferroelectric hysteresis loops of these crystals after irradiation, i.e., the crystals develop the normal loops before irradiation, but in the irradiated crystals the typical double loops are observed under higher electric field. Hence, it would be of interest to undertake an X-ray scattering measurement in order to look into the structural changes of these crystals caused by the radiation in connection with their ferroelectric properties.

The crystals used in these experiments were thin slices having thickness about 0.7 mm. They were irradiated with γ -ray from Co⁶⁰ at room temperature, and the intensity of this source is 1.9×10^6 roentgens per hour which was estimated by Fricke's method. The specimens were sealed in polyethylene envelopes during the experiments, since their physical properties are very sensitive to humidity.

Their appearances changed gradually in the course of exposure: the coloring and opacity of crystals and the evolution of water were clearly found under high dosages. The crystals were examined by X-ray method before and after a wide range of irradiations. The ferroelectric properties of these organic compounds are very sensitive to the radiation¹⁻⁴⁾, and, in the case of Rochelle salt, about 10^6 roentgens was sufficient to give a peculiar change in ferroelectric properties. In this dosage range, little or no remarkable change is observed in X-ray diffraction patterns. But the changes become more pronounced with an increase of dosage, and it seems natural that observable changes in X-ray pattern found under a sufficient large dosage might give some information about the process of damage. Moreover, it is known⁵⁾ and confirmed

by the authors that the X-ray irradiation has the similar effect as the γ -ray irradiation, but effects of the former during the X-ray measurements might be neglected under a high dosage of the latter. The most striking changes occurring in Rochelle salt on γ -ray irradiation can be seen in Laue photographs, as shown in Fig. 1. It will be seen that the diffuse spots are associated with Laue spots. The intensity of diffuse spots is enhanced with an increase of dosage. However, the Laue spots do not change appreciably. With still further increase of dosage, the Laue spots become splitted and at the same time the intensity of diffuse spots seems to become less marked.

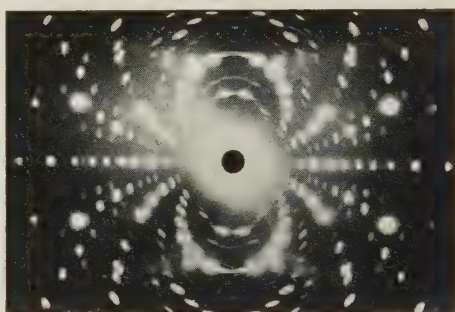


Fig. 1. Laue pattern of irradiated Rochelle salt using unfiltered copper X-radiation. Total γ -ray irradiation 3.1×10^7 roentgens. Incident X-ray beam parallel to a -axis of crystal.

We are interested in the structural change occurring in the stage where splitting of Laue spots does not yet take place, and took Laue photographs for a number of settings of crystals. It is found that the diffuse spots associated with Laue spots have neither streaks nor fine structures; in terms of the reciprocal space the scattering weights are distributed almost spherically around reciprocal lattice points. It is interesting to note that, in spite of the elimination of water molecules, the frame work of the crystal lattice remains almost unchanged. The appearance and enhancement of diffuse spots are due to the three-dimensional lattice imperfections without any directional preference which are presumably caused by the elimination of water molecules. The damage effect might be ascribed to the migration of lattice defects into the domain walls, hence clamping domain walls. More detailed studies will be reported in a near future.

We are indebted to Dr. M. Marutake of the Kobayasi Institute of Physical Research for a generous supply of Rochelle salt. It is also a pleasure to thank Professor T. Watanabé of Osaka University for his interest in this work.

References

- 1) K. Toyoda, A. Kawabata and T. Tanaka: Read

* Department of Chemistry, Konan University, Kobe.

- at the 2nd National Symposium on Atomic Energy, Feb. 1958; Read at the Annual Meeting of the Phys. Soc. Japan, May 1958 and Oct. 1959.
- 2) V. A. Iurin: *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **21** (1957) 329.
 - 3) K. Toyoda, A. Kawabata and T. Tanaka: Read at the Annual Meeting of the Phys. Soc. Japan, Oct. 1958.
 - 4) A. G. Chynoweth: *Phys. Rev.* **113** (1959) 159.
 - 5) K. Okada: *J. Phys. Soc. Japan* **15** (1960) 363.

J. PHYS. SOC. JAPAN **15** (1960) 537

Influence of Preparation and Quenching on the Magnetic Properties of Precipitates in Cu-Co Alloy

By Masayoshi SATō and Tadayasu MITUI
*Department of Physics, Faculty of Science,
University of Hokkaido, Sapporo, Japan*

(Received November 7, 1959)

In the previous study of Cu-Co alloy¹⁾, we have led to a different result from what obtained by Sucksmith *et al.*^{2),3)} on the variation of coercive force H_c with aging time. In this report, we suppose that the difference in the procedures of preparation of the sample gives the remarkable influence on the mode of precipitation. Sucksmith *et al.* have stated that the water quenching produces the surface strain which affects the rate of precipitation and have used oil quenching to avoid an irregular precipitation.

In order to find out how the variations of coercive force H_c and reverse field H_r are influenced

- by the procedure of preparation and the method of quenching, the following experiments were done.
- 1) Eventual fluctuation in H_c appeared among the samples aged at 700°C after equally treated and water quenched from 1000°C was measured. It was found that the fluctuation was less than 8 Oe and could be safely neglected.
 - 2) We used the following four samples A, B, C and D as shown in Table I. We measured H_c and H_r at room temperature of these samples quenched. The results for aging at 700°C are shown in Fig.

Table I.

sample	method of quenching	procedure of preparation
A	in water	solid solution treatment at ca. 1000°C for 1 hr after forged
B	in oil	
C	in water	solid solution treatment at ca. 1000°C for 1 hr after not forged
D	in oil	

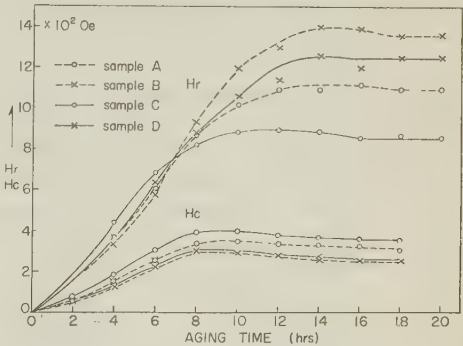


Fig. 1. Changes of H_c and H_r as a function of aging time in 2 percent Co-Cu alloy.

Table II. The ratios of the maximum values of H_c and H_r .

samples	ratios of H_c	750°C	700°C	ratios of H_r	750°C	700°C
not forged	$H_c(w)/H_c(o)$	1.36	1.29	$H_r(o)/H_r(w)$	1.30	1.40
forged	$H_c(w)/H_c(o)$	1.28	1.13	$H_r(o)/H_r(w)$	1.17	1.25
water-quench	$H_c(nf)/H_c(f)$	1.05	1.15	$H_r(f)/H_r(nf)$	1.01	1.24
oil-quench	$H_c(nf)/H_c(f)$	1.00	1.00	$H_r(f)/H_r(nf)$	0.92	1.15

(w) water quench. (o) oil quench. (f) forged. (nf) not forged.

- 1. The changes of H_c and H_r at 750°C showed also a similar behavior to each of 700°C-aging.
- As shown in Table II, it was found that the magnetic properties of Cu-Co alloy were affected not only by the method of quenching but also by the procedures in preparation of the sample before aging. It is supposed that the mode of precipitation depends upon the sample history. Accordingly, to study quantitatively the magnetic properties in these alloys, one must take care of these effects. Moreover, surface effects of quenching were also

found in the results of measurements of H_c and H_r . The detailed reports will be published in this Journal.

References

- 1) M. SATō and T. Mitui: *J. Phys. Soc. Japan* **14** (1959) 1254.
- 2) G. Bate, D. Schofield and W. Sucksmith: *Phil. Mag.* **46** (1955) 621.
- 3) B. W. Lothian, A. C. Robinson and W. Sucksmith: *Phil. Mag.* **3** (1958) 999.

J. PHYS. SOC. JAPAN 15 (1960) 538~539

Optical Bleaching of R -bands in LiF CrystalsBy Kuniya FUKUDA, Akizo OKUDA*
and Yoichi UCHIDADepartment of Physics, Faculty of Science,
Kyoto University

(Received February 2, 1960)

It has not been conclusively decided whether R -bands in alkali halides arise from the transitions in the same center or not⁽¹⁻⁵⁾. We observed the behaviors of R -bands in LiF crystals.

LiF crystals grown up in our laboratory⁶⁾ were irradiated with 1-Mev electrons from Van de Graaff machine. At the exposure of about 10^8 rad, two absorption bands at $320\text{ m}\mu$ and $380\text{ m}\mu$ were definitely observed between F - and M -bands. Overlapping these two bands, a weak and broad band appeared, but it was bleached out by a brief exposure to ultraviolet light without affecting them (Fig. 1 (a)~(b)). From the results described below, it is sure that the bands at $320\text{ m}\mu$ and $380\text{ m}\mu$ are R_1 - and R_2 -bands respectively⁷⁾.

The following results were found concerning the relations between R_1 - and R_2 -bands. (1) The relative intensities of F -, R - and M -bands after electron bombardments depended on the sample temperature under irradiations. R -bands pro-

minently appeared at about 100°C and only weakly at the temperature lower than room temperature or higher than 150°C . In this case the intensity ratios of both R -bands (R_1/R_2) were nearly constant. (2) When colored samples were exposed to the light in R -bands from carbon arc or mercury lamp through filters at room temperature, both R -bands were bleached and M -band was enhanced (Fig. 1). In spite of different intensity distribution of exposing light used in each bleaching experiment, R_1 - and R_2 -bands were bleached with a nearly constant ratio of decrements in their intensities ($\Delta R_1/\Delta R_2$), which was nearly equal to (R_1/R_2) in (1). During the bleaching of Fig. 1, in which R -bands were finally bleached out, the above ratio did not change and the peaks of the bands did not shift. (3) In the bleaching experiments using various monochromatic lights in R -bands, R -bands were more effectively reduced by R_1 -light than by R_2 -light, the decrement ratio being the same as ($\Delta R_1/\Delta R_2$) in (2). (4) When the sample scarcely exhibiting R -bands by the pre-exposure to R -light was exposed to M -light at room temperature, M -band was reduced and R -bands were almost recovered with their increment ratio equal to ($\Delta R_1/\Delta R_2$) in (2). This fact is somewhat similar to the results of KCl⁽¹⁾. The results of (2) and (3) indicate that the direct optical bleaching of the one of R -bands accompanys the bleaching of the other R -band and that the efficiency of R -bands bleaching is higher for the light in the band of higher energy side. These facts, together with the results of (1) and (4), support the suggestion by Herman and others⁽¹⁻³⁾ that R_1 - and R_2 -bands are induced from two transitions in a single center.

We observed the dichroism of R -bands at room temperature. When the sample exhibiting R -bands was irradiated with the light in R -bands polarized

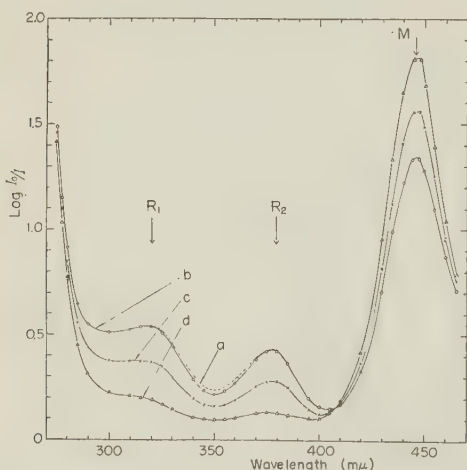


Fig. 1. Bleaching of R_1 - and R_2 -bands in an LiF crystal by R -bands light. (a) After irradiation with Van de Graaf electrons; (b) 15 minutes, (c) more 3 hours, and (d) more 12 hours exposure to Hg-lamp light through a ultraviolet filter at room temperature. Absorptions were measured at room temperature.

* Department of Mathematics and Physics, Faculty of Science and Engineering, Ritsumeikan University.

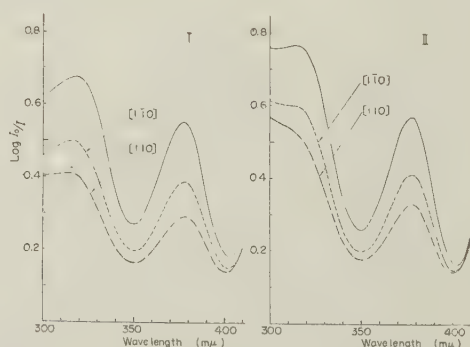


Fig. 2. Dichroism of R -bands in LiF crystals irradiated with Hg-lamp light through a ultraviolet filter (I), and with monochromatic light ($\lambda=325\text{ m}\mu$) (II), polarized along $[110]$ direction at room temperature. The measurements were made at room temperature. Solid lines show the absorptions before the irradiations.

along [110] direction, the absorption intensities of both *R*-bands polarized along [110] were more reduced than those polarized along $[1\bar{1}0]$ (Fig. 2 (I) and (II)). This is the same as the *R*-bands dichroism of KCl⁵⁾. For the irradiation with the light polarized along [100], both bands showed no dichroism in absorption along [100] and [010]. From these results it might be considered, as suggested by van Doorn³⁾, that the symmetry axis of *R*-center does not lie along $\langle 110 \rangle$ direction but along $\langle 111 \rangle$ direction, and, furthermore, the small dichroism in absorption along [110] and $[1\bar{1}0]$ seems to suggest that both *R*-bands cannot be expressed by simple optical dipoles. Finer experiments of dichroism will be reported in a near future.

The authors acknowledge the facilities offered by Dr. E. Mukoyama (Research Department, Toyo Rayon Co.) for β -irradiations.

References

1) R. Herman, M. C. Wallis and R. F. Wallis: Phys. Rev. **103** (1956) 87.

2) G. R. Cole and R. J. Friauf: Phys. Rev. **105** (1957) 1464.

3) C. Z. van Doorn: Philips Res. Rep. **12** (1957) 309.

4) J. Lambe and W. D. Compton: Phys. Rev. **106** (1957) 684. W. D. Compton and C. C. Klick: Phys. Rev. **112** (1958) 1620.

5) G. Kuwabara and A. Misu: J. Phys. Soc. Japan **13** (1958) 1066. T. Ishii, T. Tomiki and M. Ueta: J. Phys. Soc. Japan **14** (1959) 1415.

6) K. Fukuda, A. Okuda, and Y. Uchida: J. Appl. Phys. Japan **27** (1958) 535 (in Japanese).

7) C. J. Delbecq and P. Pringsheim: J. Chem. Phys. **21** (1953) 794.

Errata

Electron Microscope Study of the Decomposition
Process of Oxide Coated Cathods

By Shoichi HIROTA and Tetsuji IMAI
J. Phys. Soc. Japan **15** (1960) 137

Page	Column	Line	Wrong	Corrected
137		18	certrin	certain
"	left	41~42	encounterd	encountered
"	"	44	extremly	extremely
"	right	34	Emmission	Emission
"	"	foot note	outline	outlined
138	"	29	eace	each
"	"	48	it	It
142	"	50	100 Å	1000 Å
143	"	26~27	stated. Taht	stated that
"	"	41	perticle	particle
"	"	48	oxide.	oxides.
"	left	52~53	triple. Each	triple. In the case of triple each
"	right	35	capbonate	carbonate
144	left	34	temseratere	temperature
"	"	37	chance	change
"	right	6	parsicle	particle
138	left	Table II should be written as follows:		

Decomposition conditions		Heat treatment	
Temperature °C	Time mins	Temperature °C	Time hrs
850	15	850	5
1100	3	850	5

PROGRESS OF THEORETICAL PHYSICS

CONTENTS

Progress of Theoretical Physics	Vol. 21, No. 4, April 1959
Dynamical Properties of s - d Interaction.....	Hiroshi HASEGAWA..483
Expansion Formulae of the Free Energy and Distribution Functions in Powers of the One Particle Distribution Function.....	Tohru MORITA..501
Nuclear Photo-Reaction and Excitation Modes of Nuclei.....	Saburo FUJII..511
Quasi-Deuteron Model of Atomic Nuclei. I	Takashi TAGAMI..533
Nonlocal Interactions and Dispersion Relations	Yoshio MIYATAKE..562
Nucleon Exchange Effects in Deuteron Stripping Reactions and Angular Distri- butions of Be ⁹ (d, n) B ¹⁰ Reaction....	K. HASEGAWA and Y. H. ICHIKAWA..569
Lorentz Covariance of Quantum Electrodynamics with the Indefinite Metric..	Suraj N. GUPTA..581
Photodisintegration of the Deuteron at High Energies	Shih-Hui HSIEH..585
Electron Interaction in Very Long Linear Conjugated Molecules. I —One Dimensional Collective Oscillation of π Electrons—	Y. MIZUNO and T. IZUYAMA..593
Hydromagnetic Plane Steady Flow in Compressible Ionized Gases.....	Y. KATO and T. TANIUTI..606
On the Wave Functions of Higher Spin Particles	Shoichi HORI..613
On the Relation between the Phase Shift and the Number of Bound States	Masakuni IDA..625
On the Transformation Properties of the Dirac Equation	Pong Y. PAC..640
Letters to the Editor: A Note on the Fundamental Symmetry of Elementary Particles.....	T. OKABAYASHI..653
Isotope Shift and Fermi-Segrè Formula	N. J. IONESCO-PALLAS..655
Effect of Covalency of the Spin-Orbit Coupling Constant of Transition Metal Ions	T. MURAO..657
On Quantum Theory of Transport Phenomena	S. NAKAJIMA..659
Contents of Journ. Phys. Soc. of Japan, Vol. 14, No. 2, No. 3	660, 661
Announcement of "Supplement" to Prog. Theor. Phys., No. 7	662

Progress of Theoretical Physics	Vol. 21, No. 5, May 1959
An Analysis of the Charged Particles Emitted Following Negative Muon Absorp- tions in Photographic Emulsions	Chikai ISHII..663
On the Absorptive Range in the Pion-Nucleon Collision at High Energies....	Kin-ichi ISHIDA..676
The Imaginary Part of the Optical Potential.....	Atsushi SUGIE..681
The Electric and Magnetic Response of a Thermodynamic System	John M. BLATT and Takeo MATSUBARA..696
Two-Body Correlation of Interacting Fermions.....	Ki-ichi NAKAMURA..713
Quantum Theory in Pseudo-Hilbert Space. II	G. KONISI and T. OGIMOTO..727
Collective Excitations in Superconductors.....	Kei YOSHIDA..731
Gauge Invariance in the Theory of Superconductivity.....	J. M. BLATT, T. MATSUBARA and R. M. MAY..745
Letters to the Editor: On the Time-Variation in Thermonuclear-Fusion Systems.....	S. FUJII, M. IMOTO and G. TOMINAGA..758
Coupling Constants and the Mass Levels of Baryons	B. BRANSDEN and G. MOORHOUSE..760
Electromagnetic Structure of Nucleons	

.....K. HIIDA, N. NAKANISHI, Y. NOGAMI and M. UEHARA..	762
On the High Energy Proton Ejected in the High Energy n - d Collision	
.....Y. SAKAMOTO..	763
Statistical Nuclei with Repulsive Core Interaction.....T. ISHIDZU..	766
Errata: Dispersion Relations in Nucleon-Nucleon Scattering (Vol. 19, p. 517)	
.....S. MATSUYAMA and H. MIYAZAWA..	768
On the Exchange Magnetic Moments (Vol. 20, p. 163)	
.....E. KUROBOSHI and Y. HARA..	768

Progress of Theoretical Physics

Vol. 22, No. 1, July 1959

Thomas-Fermi-Dirac Theory with Correlation Correction.....Yasuo TOMISHIMA..	1
Pair Correlations in the Quasichemical Equilibrium Approach to Superconductivity	
.....Robert M. MAY..	12
Nucleon-Antinucleon Annihilation Products	
.....Steven C. FRAUTSCHI..	15
The Σ - N Relative Parity and the $\bar{K}$ - N Reaction.....Yukihisa NOGAMI..	25
Effect of Hard Cores on the Binding Energies of H^3 and He^3	
—Corrected Values—	
.....Takashi OHMURA..	34
Superexchange Interaction of MnO	
.....Jun KONDO..	41
Strong Fermi-Type Interaction and Its Application to the G_A/G_V Ratio in β -Decay and the Anomalous Magnetic Moment of Nucleon...Chikashi ISO..	62
Approximate Solution of the Relativistic Two-Body Equation and Its Application to the Nuclear Forces	
.....Hiroshi YAMAMOTO..	73
On the Relations between Spin Polarizations and Distorted Wave Theory of the Direct Reactions	
.....Sueji OKAI..	89
Stellar Synthesis of the α -Particle Nuclei Heavier than Ne^{20}	
.....C. HAYASHI, M. NISHIDA, N. OHYAMA and H. TSUDA..	101
Ordinary and Anomalous Thresholds in Perturbation Theory..Noboru NAKANISHI..	128
Letters to the Editor:	
Notes on Magneto-Hydrodynamic Equilibrium	
.....S. HAMADA..	145
Ambiguity in the Mixing Parameter for Nucleon Scattering.....	
.....M. KAWAGUCHI..	147
Effect of the Finite Size of the Proton on the Coulomb Energy of He^3	
.....T. OHMURA..	148
Spin-Orbit Splitting and Tensor Force.....T. TERASAWA..	150
Note on the Low Energy Electron-Hydrogen Scattering.....	
.....T. OHMURA, Y. HARA and T. YAMANOUCHI..	152
Note on the Spin-Orbit Coupling and the Tensor Forces	
.....S. TAKAGI, W. WATARI and M. YASUNO..	154
Spin-Spin Interaction in Superconductors	
.....K. NAKAMURA..	156
Errata: σ - π Interaction and Proton Hyperfine Interaction (Vol. 21, p. 779) ..	
.....S. AONO..	158
Contents of Journ. Phys. Soc. of Japan, Vol. 14, No. 5	i

Progress of Theoretical Physics

Vol. 22, No. 2, August 1959

Multipole Model of Elementary Particles. I— <i>Pion-Baryon Interactions</i> —	
.....D. ITO, S. MINAMI and H. TANAKA..	159
Multipole Model of Elementary Particles. II— <i>Non Conservation of Parity and Baryon-Lepton Interactions</i> —	
.....D. ITO, S. MINAMI, H. TANAKA, Y. TAKAHASHI and M. YAMAZAKI..	168
Nuclear Collective Motion and the Effective Two-Body Potential	
.....Y. SHONO and H. TANAKA..	177
Maximal Weak Interaction	
.....Ko AIZU..	192
Remarks on the Final State Interaction in Fermi's Theory of Multiple Particle Production	
.....Shin ISHIDA..	207
Giant Cluster Expansion Theory and Its Application to High Temperature Plasma	
.....Ryuzo ABE..	213
Effects of s - d Interaction on Transport Phenomena	
.....Tadao KASUYA..	227

Electromagnetic Structure of the Nucleon. I	
.....K. HIIDA, N. NAKANISHI, Y. NOGAMI and M. UEHARA..	247
Tensor Force of the Pion-Theoretical Potential and the Doublet Splitting in	
n -He ⁴ Scattering.....	
.....S. NAGATA, T. SASAKAWA, T. SAWADA and R. TAMAGAKI..	274
Letters to the Editor:	
High Energy n -He ⁴ Scattering.....	Y. SAKAMOTO and T. SASAKAWA..299
The Triplet Odd State Potential of the Two-Nucleon System.....	
..T. HAMADA, J. IWADARE, S. OTSUKI, R. TAMAGAKI and W. WATARI..	301
Note on Electrodisintegration of He ⁴ ..T. MUTO, T. SEBE and K. IZUMO..	304
Magnetic Susceptibility of Ce-Th Alloy	T. MURAO..307
On the Radiative Muon Decay	S. SAWADA and M. YONEZAWA..309
Possible Explanation of the Energy Gap in the Excitation Spectra of	
Nuclei	T. SASAKAWA..311
Errata: Molecular Processes induced by μ^- Mesons in Hydrogen Bubble	
Chamber. II. (Vol. 21, p. 479)	
.....Y. MIZUNO, T. IZUYAMA and M. SHIMIZU..	312
On the Wave Functions of Higher Spin Particles (Vol. 21, p. 613) ..	
.....S. HORI..	312
Contents of Journ. Phys. Soc. of Japan, Vol. 14, Nos. 6 & 7.....	i-ii

Progress of Theoretical Physics

Vol. 22, No. 3, September 1959

Charge-Transfer Forces in Molecular Compounds. II	
— <i>Benzen-Iodine Complex</i> —	Shigeyuki AONO..313
The Pion-Nucleon S -Wave Scattering, the Structure of the Nucleon and the	
Composite Model of Baryons and Mesons	Yasusi ATAKA..321
Electrical Resistance of Ferromagnetic Metals	Isao MANNARI..335
Consideration on Non-Orthogonality Catastrophe in the Heitler-London Theory.	
I	Y. MIZUNO and T. IZUYAMA..344
Electromagnetic Structure of the Nucleon. II.....	
.....K. HIIDA, N. NAKANISHI, Y. NOGAMI and M. UEHARA..	351
Possibility of Super-Weak Interactions and the Stability of Matter	
.....Yoshio YAMAGUCHI..	373
Pseudoscalar Coupling and S -Wave Pion-Nucleon and Kaon-Nucleon Scattering	
.....Reiji SUGANO..	381
Strong Interactions and Baryon Mass Levels ..B. BRANSDEN and G. MOORHOUSE..	396
Applicability Conditions of the Hydrodynamical Model of Multiple Production	
of Particles from the Point of View of Quantum Field Theory	
.....C. ISO, K. MORI and M. NAMIKI..	403
A Note on the Electromagnetic Response of Superconductors...Sadao NAKAJIMA..	430
Polaron State at a Finite Temperature.....Yukio ŌSAKA..	437
Letters to the Editor:	
On the Collective Energy Loss Mechanism of Electrons Passing through	
Solids.....	M. WATABE..447
Pions Production in Pion-Nucleon Collision with Assumption of Strong	
Pion-Pion Interaction	
.....D. ITO, M. YAMAZAKI, T. KOBAYASHI and K. MORI..	448
Branching Ratios for the K^- Capture from Hydrogen at Low Energy	
.....K. KAWARABAYASHI..	451
On a Variation Principle for Calculating the Electrical Conductivity..	
.....H. NAKANO..	453
A Proposed Model for the Explanation of the Urbach Rule..Y. TOYOZAWA..	455
Angular Distrinctions of (¹⁴ N, α) Reactions	
.....T. KAMMURI and R. NAKASIMA..	458
Energy Levels of Zr ⁹⁰ V. K. THANKAPPAN and Y. R. WAGHMARE..	459
Determination of Velocity Distribution of Electrons from Observed	
Spectral Distribution of Bremsstrahlung	

..... M. S. SODHA, C. E. STEWART and R. F. TOOPER..	461
Diamagnetism of a Dense Electron Gas.....	
..... H. KANAZAWA and N. MATSUDAIRA..	463
Effects of Potential Well Parameters on the Polarization of Elastically Scattered Protons.....	K. NISHIMURA..465
Green Function Method in Quantum-Statistics.....	
..... H. KANAZAWA and M. WATABE..	466
Errata: Molecular Processes induced by μ^- Mesons in Hydrogen Bubble Chamber. II (Vol. 21, p. 479).....	
..... Y. MIZUNO, T. IZUYAMA and M. SHIMIZU..	468
$T-Nt$ Diagram for Fusion Researches (Vol. 21, p. 939).....	
..... Y. IMOTO, G. TOMINAGA and S. FUJII..	468
The $\Sigma-A$ Relative Parity and the $\bar{K}-N$ Reaction (Vol. 22, p. 25) ..	
..... Y. NOGAMI..	468

Progress of Theoretical Physics

Vol. 22, No. 4, October 1959

2 ^3P State of Helium Atom	G. ARAKI, K. MANO and M. OHTA..	469
Dispersion Relations and High Energy Limits in Quantum Field Theory.....		
..... Seiya ARAMAKI..		485
Nucleon-Nucleon Scattering in Momentum Space: OPEP as Example.....		
..... Peter SIGNELL..		492
A Note on the Dispersion-Theoretic Approach to the One Additional Pion Pro- duction by Pion-Nucleon Collision	Kin-ichi ISHIDA..	499
The Dipole Giant Resonance in the High Energy Proton Scattering		
..... M. KAWAI and T. TERASAWA..		513
On the Inversion of the Specific-Heat Function.....	George WEISS..	526
Evolution of Massive Stars. II— <i>Helium-Burning Stage</i> —.....		
..... C. HAYASHI, J. JUGAKU and M. NISHIDA..		531
A Lower Limit on the π^0 Lifetime	Steven C. FRAUTSCHI..	544
Note on the Spin-Orbit Coupling and Tensor Forces		
..... S. TAKAGI, W. WATARI and M. YASUNO..		549
Two-Nucleon Potential with the "One-Pion-Exchange Tail".....		
.... T. HAMADA, J. IWADARE, S. OTSUKI, R. TAMAGAKI and W. WATARI..		566
Spin-Orbit Coupling and Tensor Forces.....	B. JANCOVICI..	585
Letter to the Editor:		
Photodisintegration of the Alpha-Particle.....	T. SASAKAWA..	595
Contents of Journ. Phys. Soc. of Japan ,Vol. 14, Nos. 8 & 9.....		i-ii
Announcement of "Supplement" of Prog. Theor. Phys. Nos. 9 & 10.....		iii-iv

Progress of Theoretical Physics

Vol. 22, No. 5, November 1959

Pairing Energy for Deformed Nuclei	Morikazu NOMOTO..	597
On the Possible Role of $\pi^{0\prime}$ -Meson in Decay Process		
..... S. SAWADA and M. YONEZAWA..		610
Properties of the Pion-Pion Interaction Derived from the Analysis of Pion- Nucleon Scatterings	I. SATO, A. TAKAHASHI and Y. UEDA..	617
Effect of Strange Particles on the S -Wave Pion-Nucleon Scattering		
..... A. KOMATSUZAWA, Y. NOGAMI and R. SUGANO..		638
On the Strong Interaction.....	H. MIYAZAWA, T. NAKANO and H. UMEZAWA..	643
On the Theory of Superexchange Interaction..	S. KOIDE, K. P. SINHA Y. TANABE..	647
On the Roles of Effective Interactions in Nuclear Collective Motion.....		
.. K. IKEDA, M. KOBAYASHI, T. MARUMORI, T. SHIOZAKI and S. TAKAGI..		663
Electron Interaction in Very Long Linear Conjugated Molecules. II — <i>Elementary Excitations in a System with Small Energy Gap</i> — ..		
..... Takeo IZUYAMA..		681
On the Relative Parity of Charged and Neutral K Mesons		
..... K. FUJII and H. TANAKA..		704

A Possible Symmetry in Sakata's Model for Bosons-Baryons System.....
.....M. IKEDA, S. OGAWA and Y. OHNUKI..715

Coupling Constants in β -Decay and Nucleon Structure.....Masami NAKAGAWA..725

Letters to the Editor:

On the Phase Transition of Barium Titanate Crystal W. KINASE..736

High Energy Scattering of Nucleons from Nuclei.....T. SASAKAWA..738

Some Remarks on Feynman's Variational Method.....M. NAMIKI..740

Errata: Two-Nucleon Potential with the "One-Pion-Exchange Tail" (Vol. 22,
p. 566).....H. HANADA,
J. IWADARE, S. OTSUKI, R. TAMAGAKI and W. WATARI..742

On the Representations of Field Quantities. II (Vol. 21, p. 299).....
.....H. WAKITA..743

Contents of Journ. Phys. Soc. of Japan, Vol. 14, No. 10

Price	\$ 1.25 per copy
	\$ 15.00 per year (postage inclusive)
Annual dues for foreign members (individual subscribers)	
	\$ 12.00 (postage inclusive)
for foreign members of the Physical Society of Japan	
	\$ 10.00 (postage inclusive)

Application for members, subscriptions and orders for back numbers should be sent, directly or through book-dealers, to

The Publication Office

in

Yukawa Hall, Kyoto University, Kyoto, Japan

.....

ANNOUNCEMENT

REVISED Price List of Back Numbers (for subscribers abroad)

*Vols. 1-4	\$ 6.40 each
*Vols. 5 & 6	\$13.00 each (single copy: \$2.50)
*Vols. 7 and succeeding ones	\$ 8.00 each (single copy: \$1.50)

Back number prices are effective for volumes other than last four (4) volumes (the current volume inclusive).

Thus, volumes 1 through 16 will be regarded as back numbers while volume 20 is being published.

The revised prices will be effective on and after August 1, 1958.

.....

Excitation Functions for Alpha-Induced Reactions on Manganese-55

By Shigeo TANAKA, Michiaki FURUKAWA, Takashi MIKUMO, Shiro IWATA*,
Masuo YAGI** and Hiroshi AMANO***

Institute for Nuclear Study, University of Tokyo, Tanashi, Tokyo

(Received October 1, 1959)

Excitation functions for the reactions $\text{Mn}^{55}(\alpha, n)\text{Co}^{58}$, $\text{Mn}^{55}(\alpha, 2n)\text{Co}^{57}$, $\text{Mn}^{55}(\alpha, 3n)\text{Co}^{56}$, $\text{Mn}^{55}(\alpha, \alpha'n)\text{Mn}^{54}$ and $\text{Mn}^{55}(\alpha, 2pn)\text{Mn}^{56}$ were measured by the activation method using a "stacked-foil" technique, the alpha-particle energies ranging from 10 MeV to 40 MeV. Bombardments were made with the alpha-particle beam of 32 MeV and 40 MeV from the 160 cm INSJ cyclotron. The beam was collected in a Faraday cup and measured by a current integrator. After bombardments, manganese, cobalt and iron were chemically separated. The disintegration rates of product nuclei Co^{58} , Co^{57} , Co^{56} and Mn^{54} were obtained by the gamma-ray scintillation spectrometry, while that of Mn^{56} by a calibrated end-window type Geiger counter. The reaction cross section was found to agree with calculated value for a nuclear radius constant r_0 of 1.7×10^{-13} cm. Competition between different reactions was analyzed in terms of the statistical model of nuclear reaction by use of a level density expression of $\omega = c \exp [2(aE)^{1/2}]$ and it agrees with the calculated value for $a = 2 \text{ MeV}^{-1}$.

§ 1. Introduction

A few experimental investigations have been reported on the excitation functions for the alpha-induced reactions. Most of the results can be fitted with the predictions based on the statistical model of nuclear reaction assuming the higher nuclear temperature than that obtained from the measurement of the energy spectrum of emitted particles¹⁾⁻⁵⁾. On the other hand, the angular distributions of protons emitted by the (α, p) reactions leaving the residual nuclei in low-lying states have in general forward peaks for many of the medium weight nuclei at intermediate energies. The latter fact indicates that the alpha-induced reaction leaving the residual nucleus in low-lying state proceeds by direct interaction⁶⁾.

Accumulation of more experimental data is desirable for further developments on the elucidation of nuclear reaction mechanism. This experiment is a part of the present authors' systematic study in which the cross sections of the alpha-induced reactions on

medium weight nuclei at intermediate energies are investigated.

§ 2. Experimental

Excitation functions for the reactions $\text{Mn}^{55}(\alpha, n)\text{Co}^{58}$, $\text{Mn}^{55}(\alpha, 2n)\text{Co}^{57}$, $\text{Mn}^{55}(\alpha, 3n)\text{Co}^{56}$, $\text{Mn}^{55}(\alpha, \alpha'n)\text{Mn}^{54}$ and $\text{Mn}^{55}(\alpha, 2pn)\text{Mn}^{56}$ were measured by the activation method, the alpha-particle energies ranging from 10 MeV to 40 MeV. No attempt was made to obtain the excitation function for the reaction $\text{Mn}^{55}(\alpha, 2p)\text{Mn}^{57}$ because of the short half-life of product nucleus.

1) Bombardments

The target foils were activated with the monoenergetic alpha-particle beam from the 160 cm INSJ cyclotron. The deflected beam was focused by a couple of quadrupole magnets and a sector type focusing magnet, and was collimated successively by narrow carbon slits. Energy dependence of the cross sections was measured by using the "stacked-foil" technique in which target foils were interspaced with aluminum absorbers. The energies of alpha-particles just entering and leaving each target foil were determined by calculating the energy loss in each foil and absorber in the stack. The $-dE/dx$ value in aluminum absorber was obtained from the

* Faculty of Science, Osaka University.

** Radiochemical Laboratory, Shizuoka University.

*** The Research Institute for Iron, Steel and Other Metals, Tohoku University.

range-energy curve of Aron et al.⁷⁾, and that in manganese target from the stopping power formula of Bethe et al.⁸⁾ using the estimated mean excitation potential $I=11.5 Z$ (kev) and $Z=25$.

The bombardments were performed with the alpha-particles of about $0.25 \mu\text{A}$ and 40 MeV for 4 hours and with those of $0.5 \mu\text{A}$ and 32 MeV for 3 hours. The energy spread of incident beam was estimated to be less than $\pm 1\%$. The change in cyclotron frequency during the bombardment was monitored and estimated to be less than $\pm 0.5\%$. The manganese target foil of about 3 mg/cm^2 was prepared by evaporating manganese metal onto 20μ thick aluminum foil which was pretreated with a surface active agent. The purity of the manganese metal was approximately 99.9%. With some exceptions, the inhomogeneity of manganese foil was estimated to be $\pm 7\%$ in thickness. The $3 \text{ cm} \times 3 \text{ cm}$ foils were used for cyclotron bombardment, when the section of the beam was about 0.5 cm^2 . The foils were wide enough to intercept all the beam, including the multiply scattered portion of alpha-particles. The beam was collected in a Faraday cup and the total charge of the beam was measured by a 100% feed-back type current integrator.

2) Chemical procedures

After bombardment, the target foil was dissolved in fuming nitric acid. Aluminum backing remained undissolved by this treatment. The solution was evaporated to dryness on a sand bath. The residue was dissolved in 1 ml. of 7 N HCl and passed through a column (7 mm dia. $\times$ 7 mm high) of the anion exchange resin Dowex -1×8 (200~250 mesh) followed by washing with about 10 ml. of 7 N HCl. Manganese was not adsorbed, while cobalt was strongly adsorbed at the top of the column, and was successively eluted with 4 N HCl (within 10 ml.). Each fraction was adjusted to 5 ml. and aliquots were taken for counting. The sample for gamma-ray measurement was prepared by taking 2 ml. of each fraction in a polyethylene vessel. One ml. of the manganese fraction was evaporated in a glass counting dish and oxidized to manganese dioxide by heating with a small amount of nitric acid to be used for Geiger counting. The sample for $4\pi\beta$ -counting was prepared by taking a definite small portion of the solu-

tion with a micropipette onto a gold-spattered polyvinyl acetate film supported by an aluminum holder.

3) Counting procedures

(a) $\text{Mn}^{55}(\alpha, 2p_n)\text{Mn}^{56}$ The activity of each manganese sample was counted with an end-window type Geiger counter whose geometry had been calibrated with various beta-emitters. The disintegration rate and the relative yield were obtained by analyzing the decay curve. Small corrections for self-absorption and self-scattering were made.

(b) $\text{Mn}^{55}(\alpha, \alpha'n)\text{Mn}^{54}$ After Mn^{56} had decayed completely, the activity of each manganese sample was measured in a well-type NaI(Tl) scintillation spectrometer. The relative yield was obtained from the photo-peak of 0.842 MeV gamma-ray from Mn^{54} . The disintegration rate was given by comparing the sample with the Mn^{54} standard source. The Mn^{54} standard source had been measured by use of a 1-3/4 in. dia. $\times$ 2 in. high NaI (Tl) crystal in a poorly defined geometry and the photo-peak efficiency had been applied to the counting rate.

The photo-peak efficiency ϵ_p was calculated from the equation $\epsilon_p = R\epsilon_i\Omega_e$. The values of calculated efficiency $\epsilon_i\Omega_e$ of the 1-3/4 in. dia. $\times$ 2 in. high NaI(Tl) crystal were obtained from the work of Wolicki et al.⁹⁾ and those of peak-to-total ratio R from the work of Berger et al.¹⁰⁾

(c) $\text{Mn}^{55}(\alpha, n)\text{Co}^{58}$ The gamma-ray spectrum of each cobalt sample (the typical one is shown in Fig. 1.) was examined by means of a 2 in. dia. $\times$ 2 in. high NaI(Tl) scintillation spectrometer. The change in spectrum was followed every 4 hours with the aid of a 10

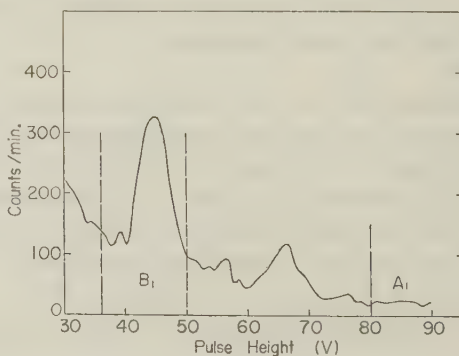


Fig. 1. Gamma-ray scintillation pulse height spectrum of the cobalt sample.

channel pulse height analyser.* After Co^{58m} had decayed to Co^{58} , the relative yield of $Co^{58m+58g}$ was obtained from the photo-peak of 0.814 MeV gamma-ray, the contribution from Co^{56} (produced by the reaction $Mn^{55}(\alpha, 3n)Co^{56}$) being subtracted. The subtraction procedure is given below. The gamma-ray spectrum of Co^{56} standard source (produced by the proton bombardment of natural iron) was also taken and is shown in Fig. 2. Output signals from the amplifier above 80 V (Fig. 1. and Fig. 2.) are named A_1 and A_2 , and those from 36 V to 50 V are named B_1 and B_2 . As A_1 is supposed to be from Co^{56} , the value of $(B_1 - A_1 B_2 / A_2)$ gives the photo-peak count from Co^{58} only. The disintegration rate was obtained by comparing the 0.814 MeV photo-peak of the sample which was bombarded below the threshold of $(\alpha, 3n)$ reaction with the 0.842 MeV photo-peak from Mn^{54} standard source. It was cross-checked by a $4\pi\beta$ -counting.

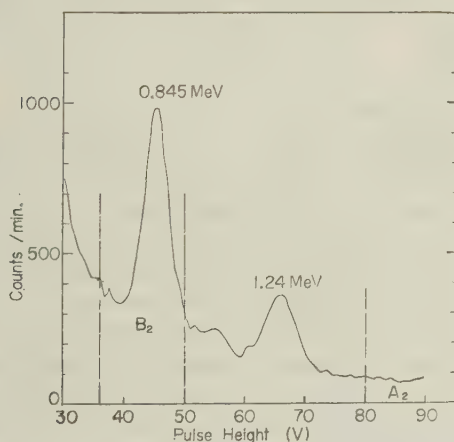


Fig. 2. Gamma-ray scintillation pulse height spectrum of Co^{56} standard source.

The cross section for isomer formation and that for ground-state formation were separately measured. The result of the yield ratio for isomeric pair is to be published in near future.

(d) $Mn^{55}(\alpha, 3n)Co^{56}$ Counting method was the same as in the case of $Mn^{55}(\alpha, n)Co^{58}$. The relative yield was obtained by taking the surplus count above 80 V of the amplifier

signals in Fig. 2 (which corresponds to gamma-rays above 1.5 MeV). This procedure discriminates the gamma-rays from the other cobalt activities. The disintegration rate was obtained by comparing the sample with the Co^{56} standard source. The Co^{56} standard source was calibrated by comparing the 0.845 MeV photo-peak with 0.842 MeV photo-peak from Mn^{54} standard source, and was cross-checked by a $4\pi\beta$ -counting.

(e) $Mn^{55}(\alpha, 2n)Co^{57}$ The activity of each cobalt sample was measured in a well-type NaI(Tl) scintillation spectrometer. The disintegration rate and the relative yield of Co^{57} were obtained from the photo-peak at 0.122 MeV gamma-ray. Compton tails from more energetic gamma-rays were subtracted graphically in each spectrum. The counting efficiency of the crystal** for the 0.122 MeV gamma-ray was estimated to be 0.85, which had been corrected for geometrical loss and absorption loss in the aluminum cover and in the aluminum oxide light reflector.

4) Correction of "recoil loss"

The gamma-ray spectrum of the aluminum backing foil indicated the presence of a considerable amount of Co^{58} and the other activities which seemed to be produced by the alpha-induced reactions on manganese. Manganese was not detected in the aluminum foil by a colorimetric analysis. The activities in the aluminum foil were estimated to be the product nuclei recoiled from the manganese target. Attempts were made to find the amount of "recoil loss" from the target. Aluminum backing foil was chemically separated by nearly the same procedures as in the case of the manganese target, and similarly submitted to counting. The amounts of "recoil loss" for each reaction were thus obtained as a function of the alpha-particle energy. They were about 20% of total activities produced for the evaporated target foil, and were used for the corrections of relative and absolute yields. The "recoil loss" for $(\alpha, 2pn)$ reaction was not obtained, because the short-lived product nucleus had decayed before counting. The "recoil loss" correction for the $(\alpha, 2pn)$ reaction was per-

* All the electronic equipments including a Johnston type 10 channel pulse height analyser were developed and constructed in the Electronics Division of this Institute.

** 1-3/4 in. dia. $\times$ 2 in. high Harshaw's 7F8 well-type NaI(Tl) crystal with a hole 3/4 in. dia. $\times$ 1-1/2 in. depth and with a spun aluminum well cap 0.032 in. thick.

formed by use of the value for $(\alpha, 3n)$ reaction.

§ 3. Results

The cross sections were calculated in a direct manner using the nuclear data shown in

Table I. Nuclear data necessary for the calculation.

Nuclide	Half-life	Radiation and Energy	Emission probability of beta- and gamma-ray (%)
Co ⁵⁸	71d	β^+ 0.485 MeV	15
		γ 0.814 MeV	100
Co ⁵⁷	270d	γ 0.122 MeV	100
		γ 0.138 MeV	
Co ⁵⁶	77d	β^+ 1.50 MeV	20
		β^+ 1.00 MeV	
		β^+ 0.44 MeV	
		γ 0.845 MeV	100
Mn ⁵⁸	2.58h	β^- 2.81 MeV	50
		β^- 1.04 MeV	30
		β^- 0.65 MeV	20
Mn ⁵⁴	290d	γ 0.842 MeV	100

Table I. These data were obtained from the compilation of Strominger et al.¹¹⁾ and from the newer nuclear data in literatures.¹²⁾ The absolute cross sections are plotted as a function of alpha-particle energy in Fig. 3, together with the energy width in target foil and with the estimated standard error of the magnitude of cross section for some experimental points.

The cross section calculation is very sensitive to the decay scheme of residual nucleus. The plotted cross section for (α, n) reaction was calculated from the disintegration rate obtained by the gamma-ray measurement and it was about 15% smaller than that by the $4\pi\beta$ -counting assuming that the emission probability of positrons in Co⁵⁸ is 15% of the total disintegration. The plotted cross section for $(\alpha, 3n)$ reaction was also calculated from the gamma-ray measurement and it was about 33% smaller than that from $4\pi\beta$ -counting. As the positron emission probability of Co⁵⁶ is at present somewhat uncertain, the value from $4\pi\beta$ -counting does not seem to be fully reliable.

§ 4. Discussion

Excitation functions were compared with the predictions based on the statistical model using the following assumptions.

- (1) It was assumed that neutrons, protons and alpha-particle were the only particles involved. The evaporation of deuterons would increase the (α, pn) reaction cross section but this type of process appears to be negligible because of their small probability of existence at the nuclear surface and the difficulty in penetrating the Coulomb barrier¹³⁾. Tritons would be in the same situation as deuterons.
- (2) The cross section for the formation of compound nucleus, including that for the inverse process was taken from Shapiro's calculation¹⁴⁾. It was assume that an alpha-particle had a finite size and the interaction radius R was expressed as $R=(r_0\times A^{1/3}+1.21)\times 10^{-13}$ cm for an alpha-particle and $R=r_0\times A^{1/3}\times 10^{-13}$ cm for a nucleon.
- (3) The level density ω of residual nucleus was assumed to be given by the expression $\omega=c\exp[2(aE)^{1/2}]$, in which a and c were constants. The value of a chosen was 2 MeV⁻¹, which was in fair agreement with many measurements of excitation functions

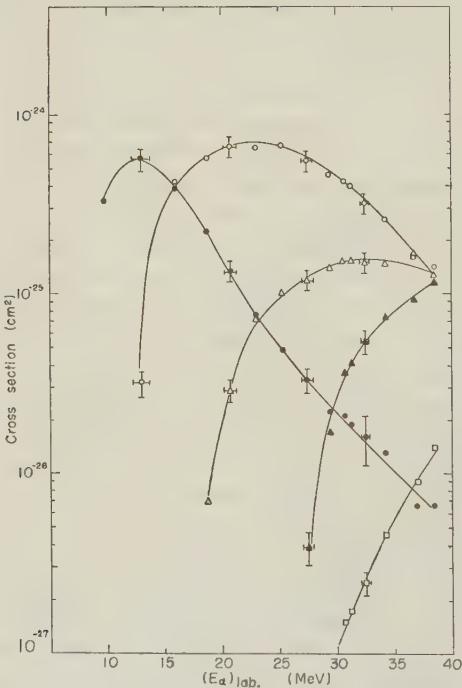


Fig. 3. Excitation functions for the alpha-induced reactions on Mn⁵⁵.

- Mn⁵⁵(α, n)Co⁵⁸
- Mn⁵⁵($\alpha, 2n$)Co⁵⁷
- ▲ Mn⁵⁵($\alpha, 3n$)Co⁵⁶
- △ Mn⁵⁵($\alpha, \alpha'n$)Mn⁵⁴
- Mn⁵⁶($\alpha, 2pn$)Mn⁵⁶

with alpha-particles⁵⁾. The dependence of level density on an odd-odd, an odd-even, an even-odd and an even-even nucleus was taken into account as follows¹⁵⁾.

$$\frac{\omega_{o-o}}{12} \sim \frac{\omega_{o-e}}{5} \sim \frac{\omega_{e-e}}{1} \quad \omega_{o-e} = \omega_{e-o}.$$

(4) De-excitation by photon emission was

Table II. Binding energies.

	Binding energy in MeV		
	<i>B_n</i>	<i>B_p</i>	<i>B_α</i>
Co ⁵⁹	10.2	7.2	6.8
Co ⁵⁸	8.3	7.0	6.7
Co ⁵⁷	11.7	6.3	7.4
Co ⁵⁶	10.0	5.8	7.8
Mn ⁵⁵	10.1	8.1	7.9
Mn ⁵⁴	9.1	7.7	9.0

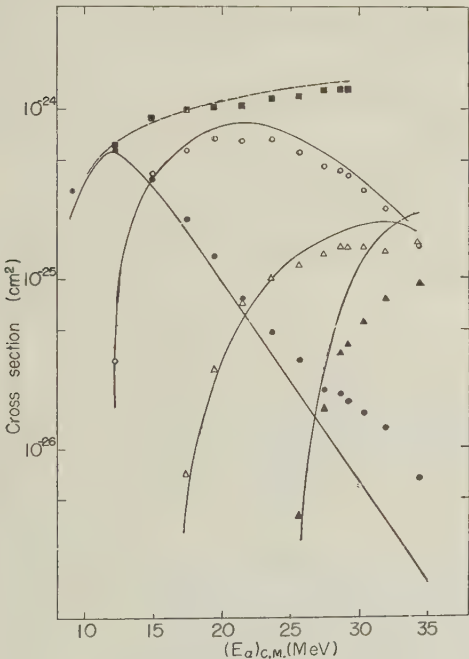


Fig. 4. Comparison of experimental and theoretical results for the cross sections of the alpha-induced reactions on Mn⁵⁵.

- Mn⁵⁵(α, n)Co⁵⁸
▲ Mn⁵⁵(α, 3n)Co⁵⁶
○ Mn⁵⁵(α, 2n)Co⁵⁷
△ Mn⁵⁵(α, α'n)Mn⁵⁴
■ Total reaction cross section from the measured and the estimated values of most probable reactions.
— Theoretical value for each reaction.
--- Shapiro's calculation of r₀=1.7.

} Experimental data

assumed to be allowed for by shifting the threshold for the secondary proton emission upward by 2 MeV^{16), 17)}.

(5) The emission probabilities are very sensitive on the binding energies of various particles. The values of binding energy were obtained from the compilation of Wapstra¹⁸⁾; those used in this calculation are listed in Table II.

The results of calculation are shown in Fig. 4, along with the experimental data. Agreements between them are good both for the magnitude of cross section and for the shape of excitation function. The cross section of compound nucleus formation obtained from the measured cross sections and from the estimated values for the reactions leading to stable nuclei is consistent with a nuclear radius constant *r*₀ of 1.7. This agrees well with the results obtained by the present authors in the alpha-induced reactions on iron-54 and nickel-58¹⁹⁾. The competition between different reactions is well fitted with the statistical model calculation with the five assumptions. However, the magnitude of the cross section for (α, 3*n*) reaction is not completely reproduced by the calculation.

Acknowledgements

Authors' thanks are due to Prof. I. Nonaka and the other members of staff of Low Energy Division in this Institute for their interest and encouragement. They are also grateful to the Cyclotron Crew for their cyclotron operation.

References

1) G. M. Temmer: Phys. Rev. **76** (1949) 424.
2) E. Bleuler, A. K. Steffins and D. J. Tendam: Phys. Rev. **90** (1953) 460.
3) K. G. Porges: Phys. Rev. **101** (1956) 225.
4) N. T. Porile: Phys. Rev. **115** (1959) 939.
5) G. Igo and H. E. Wegner: Phys. Rev. **102** (1956) 1364.
6) I. Nonaka et al.: to be published in J. Phys. Soc. Japan.
7) W. A. Aron, B. G. Hoffman and F. C. Williams: U. S. Atomic Energy Commission Report. AECU-663 (1949).
8) M. S. Livingston and H. A. Bethe: Rev. Mod. Phys. **9** (1937) 245.
9) E. A. Wolicki, R. Jastrow and F. Brooks: Naval Research Laboratory (U.S.) Report. No. 4833 (1956); *Handbuch der Physik*, vol. **45** (Springer-Verlag, 1958) 126.

- 10) M. J. Berger and J. Doggett: J. Res. Nat. Bur. Stand. **56** (1956) 355.
- 11) D. Strominger, J. M. Hollander and G. T. Seaborg: Rev. Mod. Phys. **30** (1958) 585.
- 12) C. S. Cook and F. M. Tomnovec: Phys. Rev. **104** (1956) 1407.
- 13) K. Kikuchi: Progr. Theor. Phys. **18** (1957) 503.
- 14) M. M. Shapiro: Phys. Rev. **90** (1953) 171.
- 15) G. Brown and H. Muirhead: Phil. Mag. **2** (1957) 473.
- 16) J. W. Meadows: Phys. Rev. **98** (1955) 744.
- 17) D. L. Allan: Proc. Phys. Soc. London **A, 70** (1957) 195.
- 18) A. H. Wapstra: *Handbuch der Physik*, vol. **38-1** (Springer-Verlag, 1958) 1; *Physica* **21** (1956) 367.
- 19) S. Tanaka et al.: to be published in J. Phys. Soc. Japan.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

Differential Cross Sections for the Reaction $C^{12}(d, p)C^{13}$ in the Energy Range of Deuterons from 15- to 20-MeV*

By Susumu MORITA, Nawoyuki KAWAI, Naoyuki TAKANO,
Yorio GOTÔ, Reiko HANADA,

Department of Physics, Kyushu University, Fukuoka

Yutaka NAKAJIMA,

Department of Physics, University of Tokyo, Tokyo

Shigeo TAKEMOTO and Yûki YAEGASHI

Department of Physics, Tôhoku University, Sendai

(Received October 30, 1959)

The angular distributions of protons from the reaction $C^{12}(d, p)C^{13}$ were measured at the deuteron energies of 14.9-, 16.6-, 18.1-, and 19.6-MeV, for the proton groups leading to the lowest four levels of C^{13} . The proton groups to the second and third excited states were not resolved. The measurements covered the angular range from 15 to 165 degrees at intervals of 7.5 degrees. The results were compared with the stripping theory and qualitative agreement in the forward directions was obtained, but not in the backward.

The best fits for the angular distributions of the ground state group were obtained with the nuclear radius of $(6.3 \pm 0.1) \times 10^{-13}$ cm with Bhatia's formula. The angular distributions changed regularly with the deuteron energy. The excitation function was found to decrease monotonically with the increase of deuteron energy but that in the backward directions showed a slower decrease than that for the forward directions.

§ 1. Introduction

The reaction $C^{12}(d, p)C^{13}$ is one of the most well-studied nuclear reactions and the angular distributions of protons from this reaction have been almost thoroughly investigated in the range of deuteron energy below 6 MeV.¹⁾

* This experiment was performed with the 160 cm variable energy cyclotron at the Institute for Nuclear Study, University of Tokyo.

Nevertheless, the reaction mechanism has not yet been well understood. For example, the excitation curve at the deuteron energy above 4 MeV, obtained at some definite angles, showed remarkable maxima and minima, in contrast to the stripping type of angular distributions in the same energy region. Although these maxima and minima in the excitation curve may not be directly related

to the resonances in the compound nucleus formation, the simple stripping theory will not be able to explain these maxima. In the range of deuteron energy above 9 MeV, the angular distribution measurements has been made at 9 MeV by Green and Middleton²⁾, at 14.8 MeV by McGruer *et al.*³⁾, at 19 MeV by Freemantle *et al.*⁴⁾, and at 24 MeV by Conzett *et al.*⁵⁾.

At these higher energies of deuterons, the angular distributions could be fitted qualitatively to the Butler's stripping theory, but the agreements for C^{12} seem not to be satisfactory, while the good agreements have been obtained in these higher energy ranges for other light nuclei. Moreover, except the experiment of Freemantle *et al.*⁴⁾, the measurements were confined only in the forward directions. We intended to investigate the variation of the angular distributions for the deuteron energies from 15- to 20-MeV in the angular range from 15 to 165 degrees. The angular distributions in the backward directions can not be obtained by the stripping theory and will be interesting in relation to the recent direct interaction theory by Butler *et al.*⁶⁾. Moreover, the variation of total cross sections, obtained by integration of the angular distributions, with the deuteron energy, will give some information about the reaction mechanism in these energy ranges.

§ 2. Experimental Procedure

The experimental arrangement is shown in Fig. 1 and is quite similar to the arrangement used in the study of (α, p) reactions by Nonaka *et al.*^{*7)}.

The deuteron beam from the cyclotron was collimated by two defining slits of graphite of 5 mm in diameter and 80 cm apart, and between these two slits, three antiscattering graphite baffles of 8 mm diameter were arranged equidistantly. The beam energy spread was estimated to be within about 0.5 % at the target. The target of self-supporting film of elemental carbon were prepared from colloidal solution of graphite and the thickness was measured to be 2.04 mg/cm^{2**} .

* We are indebted to Prof. Nonaka *et al.* for the use of the detector systems they had made.

** We are indebted also gratefully to Mr. Mikumo of Institute for Nuclear Study for the preparation of the target.

This target was ascertained to be quite uniform and contain no detectable impurities except hydrogen, which was absorbed as humidity.⁷⁾ The target was set in such a way that its surface makes 45 degrees to the deuteron beam. The two sets of scintillation counters and cathode followers were arranged in the opposite directions to the target so as to measure the counts at two angles in the forward and backward directions simultaneously, and were rotated around the target with the turn table in the scattering chamber,

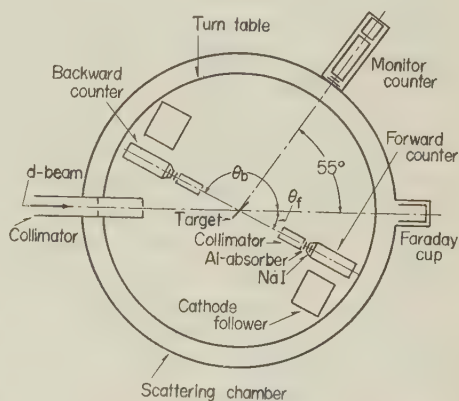


Fig. 1. Schematic diagram of scattering chamber.

whose inner diameter was 100 cm. The counts in the two counters were normalized at the direction of 90 degrees. The scintillators of CsI or NaI crystals used were 3 and 2 mm thick in the forward and backward counters, respectively. These scintillators were coupled with the Du Mont 6467 photomultipliers and four 20 channel pulse height analysers, of which each two sets were used in series as a 40 channel analyser. The energy resolution of these counters was 3 to 5 percent, as can be seen in Fig. 2. As is shown in Fig. 1, a collimator of circular opening was arranged for each counter to define the solid angle of the order of 10^{-4} steradians subtended by the counter, and an absorber of aluminium of 600 micron thickness, set just before each counter window, served to discriminate the deuterons scattered by the target and the alpha particles from any reactions. With these detector arrangements, the proton groups leading to the several low-lying levels of C^{13} were separated from background. The thicknesses of scintillators chosen were enough to stop all the

protons from the (d, p) reaction.

The measurements were made in the range of angle from 15 to 165 degrees at intervals of 7.5 degrees. The monitor counter was arranged at the direction of 55 degrees to the deuteron beam and the protons entered to the

scintillator of CsI of 3 mm in thickness through an aluminium foil in the side wall of the scattering chamber. The single channel pulse height analyser coupled with the monitor counter was biased so as to discriminate all the pulses smaller than those due to the protons of ground state group and, thus, the effect of drift of the bias level of this analyser was minimized. The deuteron beam was collected by a Faraday cup and was measured with an current integrator. The proportionalities between the counts in the monitor counter and those in the current integrator were constant within 2.6 percent. The angular distributions were obtained by referring to the monitor counts, and the absolute values of the differential cross sections and the excitation curve were estimated referring to the counts in the current integrator. For the determination of the energy of deuteron, a small fraction of the beam was extracted through a hole in the Faraday cup and the range in aluminium was measured according to the method of Mather and Segré⁸⁾.

§ 3. Results and Discussion

Some examples of the pulse height spectra of protons are shown in Fig. 2. At lower energies of deuteron and in the backward directions, the energies of emitted protons get lower and the proton peaks in pulse height spectra overlapped on or smeared out into the γ -ray background. The arrows in Fig. 2 (a) show the energies of protons leading to the ground and excited states of C^{13} at 3.09-, 3.69-, and 3.86-MeV⁹⁾, calculated by the reaction kinematics. These energies were in good agreement with the positions of the peaks obtained and the variations of energies at these peaks with angles were also consistent with the protons from the $C^{12}(d, p)C^{13}$ reaction. The proton groups leading to the ground state and to the first excited state are well separated from each other, but those to the second and to third excited state could not be resolved, and the angular distributions of the mixture of these two groups were obtained. The angular distributions, thus obtained, are illustrated in Fig. 3, 5 and 6. The statistical errors of each point were smaller than 2.6 percent and were negligible in these figures. The background was smal-

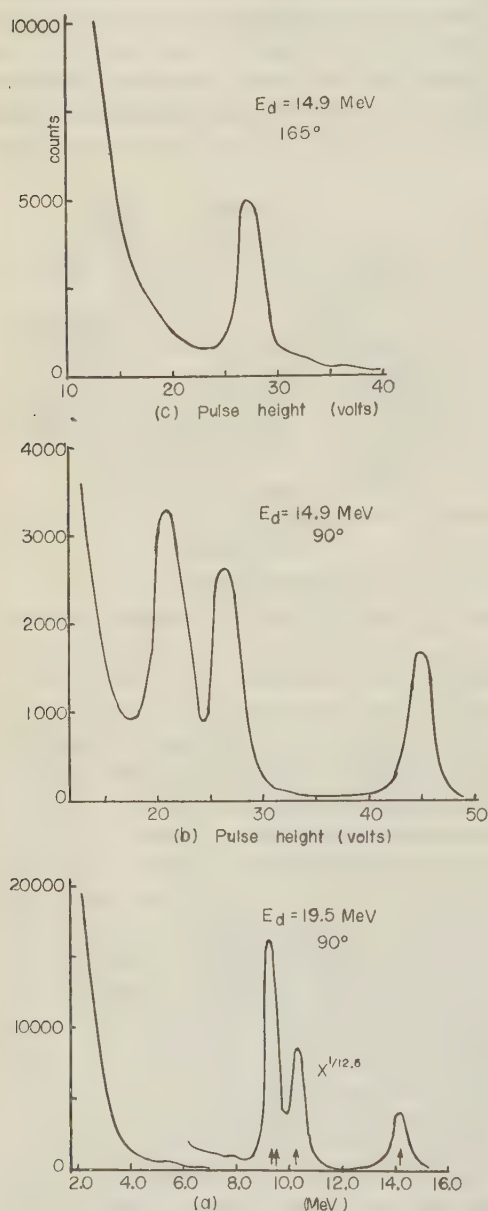


Fig. 2. (a) shows the energy spectra of protons from the $C^{12}(d, p)C^{13}$ reaction, obtained at 90° (lab. system) with $E_d=19.5$ MeV. The arrows show the calculated energies of proton groups to the ground, 3.09-, 3.69-, and 3.86-MeV levels. (b) and (c) show the pulse height spectra of protons, observed at 90° and 165° (lab. system), respectively, with $E_d=14.9$ -MeV.

ler in higher energies of deuteron and in forward directions, where it was usually 5.1 percent and became larger at lower energies and in the backward directions and the errors in the estimation of the background amounted to 7.8 percent at maximum. Another uncertainty came from group separation in the energy spectra, and it amounted to 4.8 percent at maximum, when the deuteron energy was the lowest. The angular distributions for the ground state group, taken at the deuteron energies of 14.9-, 16.6-, 18.1-, and 19.6-MeV, are shown in Fig. 3. The dotted curves in this figure show the stripping curves calculated by using the formula obtained by Bhatia *et al.*¹⁰⁾ with $l_n=1$ and $r_0=6.3 \times 10^{-13}$ cm. As the spins and parities of the ground states of C^{12} and C^{13} are $0+$ and $1/2-$, respectively, the stripping process with $l_n=1$ is considered to be predominant. The theoret-

tical curves in the extremely forward directions, which are not shown in this figure, reach maxima at 0 degree after increasing rapidly. The experimental data could not be obtained in these angular range. The cross sections at the second maxima of the theoretical curves at about 50 degrees were normalized to the experimental maxima at these angles. The best fit of these maxima to the experimental data was obtained with $r_0=(6.3 \pm 0.1) \times 10^{-13}$ cm. Although this value of nuclear radius is somewhat larger compared with those of other light nuclei obtained by (d, p) reactions, it may not be so unreasonable. The angular distributions obtained by McGruer *et al.*³⁾ at 14.8 MeV and by Freemantle *et al.*⁴⁾ at 19.1 MeV, which were normalized to our data at the maxima, are also shown in these figures, showing good agreement with the present data within their experimental errors. The scale of the ordinate of these figures, has an uncertainty of about 20 percent, owing to the unknown content of the molecular hydrogen ion in the deuteron beam and the absolute value of the cross section is in agreement with that obtained by McGruer *et al.*³⁾ within the experimental error. From these figures, it is found that the general behaviors of experimental curves are consistent with the stripping theory but rather regular changes with deuteron energy are found in the experimental curves. First, the maxima at about 50 degrees in the experimental curves become less pronounced with the increase of deuteron energy. Secondary, the increase of the differential cross sections in the backward directions becomes remarkable as the deuteron energy decreases. As the compound nucleus formation will little contribute to this reaction at these higher deuteron energies, the rise in the backward directions will be attributed to the heavy particle stripping¹¹⁾ or to the direct interaction process suggested by Butler *et al.*⁶⁾. The total cross sections for the ground state group, estimated by integration over the angular range from 15 to 165 degrees, are plotted against the deuteron energy and are shown by the curve A in Fig. 4. The contributions of the extremely forward range, where the experimental data were not obtained, to the total cross sections were estimated by the extrapolation of the

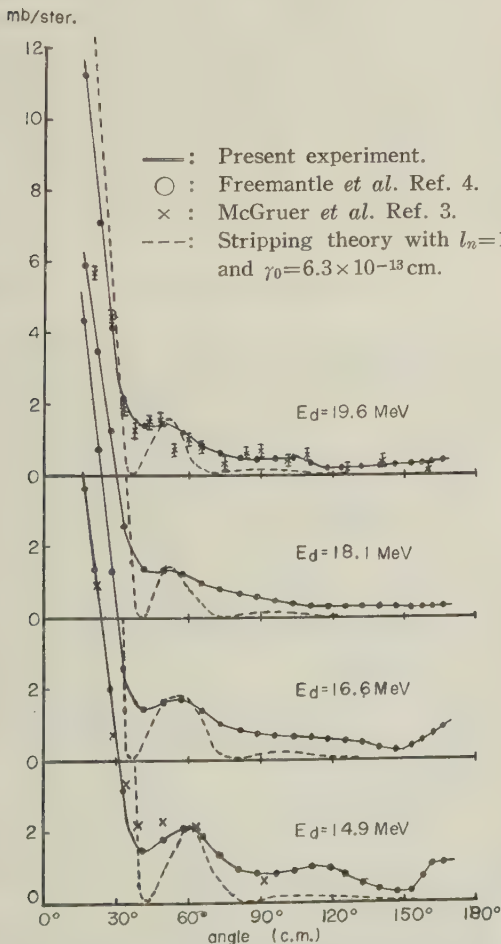


Fig. 3. Angular distributions of protons from the $C^{12}(d, p)C^{13}$ ground state reaction.

experimental angular distributions and also with the aid of the theoretical stripping curve and it was found that, by taking into account these contributions, the cross sections became larger by 14 percent than that shown by the curve A but no significant change in the general behavior was found. The curve B in Fig. 4 was calculated according to the theory of compound nucleus formation. In this calculation, the cross section for formation of the compound nucleus was assumed to be independent of deuteron energy. Then, the excitation curve for a single proton group leading to a discrete level of residual nucleus will be, principally, determined by competition between this level and all other levels of the residual nucleus. The decay probability of the compound nucleus by emitting a proton of kinetic energy between ε' and $\varepsilon' + d\varepsilon'$ can be expressed by

$$\varepsilon' \sigma_o(\varepsilon') \omega(\varepsilon^* - \varepsilon') d\varepsilon', \quad (1)$$

where $\varepsilon^* = \varepsilon + Q$ and ε is the kinetic energy of incident deuteron in the center-of-mass system and Q is the energy release in the ground state reaction. $\sigma_o(\varepsilon')$ is the cross section for the formation of a compound nucleus by a collision with energy ε' between proton and nucleus C^{13} excited at the energy $\varepsilon^* - \varepsilon'$. $\omega(E) = 0.3 \exp[2(0.3E)^{1/2}]$ is the level density of C^{13} at excitation energy E . Accordingly, the energy dependence of the cross section for formation C^{13} in its ground state is given by

$$\sigma(\varepsilon) \propto \frac{\varepsilon^* \sigma_o(\varepsilon^*)}{\int_0^{\varepsilon^*} \varepsilon' \sigma_o(\varepsilon') \omega(\varepsilon^* - \varepsilon') d\varepsilon'} \quad (2)$$

and is shown by curve B.

On the other hand, the stripping theory can not predict the excitation curve exactly because of the unknown dependence of the nuclear wave function on the deuteron energy. But, neglecting this nuclear factor, the energy dependence of the stripping cross section is determined by the energy dependence of the probability that the neutron captured by the nucleus can be found in the deuteron with proper energy and angular momentum and can be expressed by

$$\sigma(\theta) \propto \frac{k_p}{k_d} G^2 \cdot j_1^2(kR), \quad (3)$$

where the symbols have their usual meaning as are used in the stripping theory.¹⁰⁾ The curve C, thus obtained, is shown in Fig. 4. The ordinates of curves B and C are arbitrary. No significant difference was found between the curves B and C in these ranges of deuteron energy, although the curve B shows much more rapid increase than the curve C with the decrease of deuteron energy in the range below 14 MeV. The curve D in Fig. 4 shows the experimental cross sections obtained by integration over the range from 90 to 165 degrees, where the theoretical stripping cross section are negligible compared with the experimental one.

The angular distributions of protons from the $C^{12}(d, p)C^{13}$ 3.09 MeV level are shown in Fig. 5, together with the data obtained by other investigators.

The peaks in the energy spectra corresponding to this proton group, obtained at lower energies of deuteron, were masked by the γ -

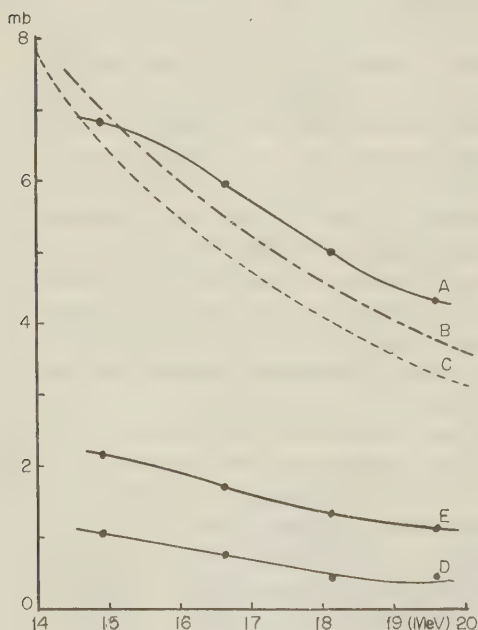


Fig. 4. Excitation curves for the $C^{12}(d, p)C^{13}$ reaction. Curve A shows the cross section for the ground state group integrated over the angular range from 15 to 165 degrees. Curve B and C show approximate theoretical excitation curves calculated by the compound nucleus formation and stripping theory, respectively. Curve D shows the experimental cross sections for the ground state group integrated over the range from 90 to 165 degrees and curve E shows those for the first excited state group integrated over the range from 60 to 90 degrees.

ray background in the backward directions, and the angular distributions in these region could not be obtained. As the spins and parities of initial and final states for this reaction has been found to be $0+$ and $1/2+$, respectively, the stripping process with $l_n=0$ must be predominant. It must be noted that the distribution in the forward region, obtained by Freemantle *et al.* $E_d=19$ MeV, is not consistent with the present data and the theoretical curve. The dotted curves show

the theoretical curves calculated by using Bhatia's formula. Better fits to experimental curve were obtained with a slightly decreasing values of nuclear radius with increasing deuteron energy, as are shown in these figures. As in the case of ground state reaction, the general behaviors of angular distributions are consistent with the stripping theory. In order to obtain some information on the protons emitted in the angular range near 90 degrees, the cross sections integrated over the angular range from 60 to 120 degrees, where the stripping cross section is quite small, is shown in Fig. 4 by the curve E. It is remarkable that the curve E shows much slower decrease with the increase of deuteron energy and behaves quite similarly with curve D. Fig. 6 shows the angular distributions of the mixture of proton groups to the

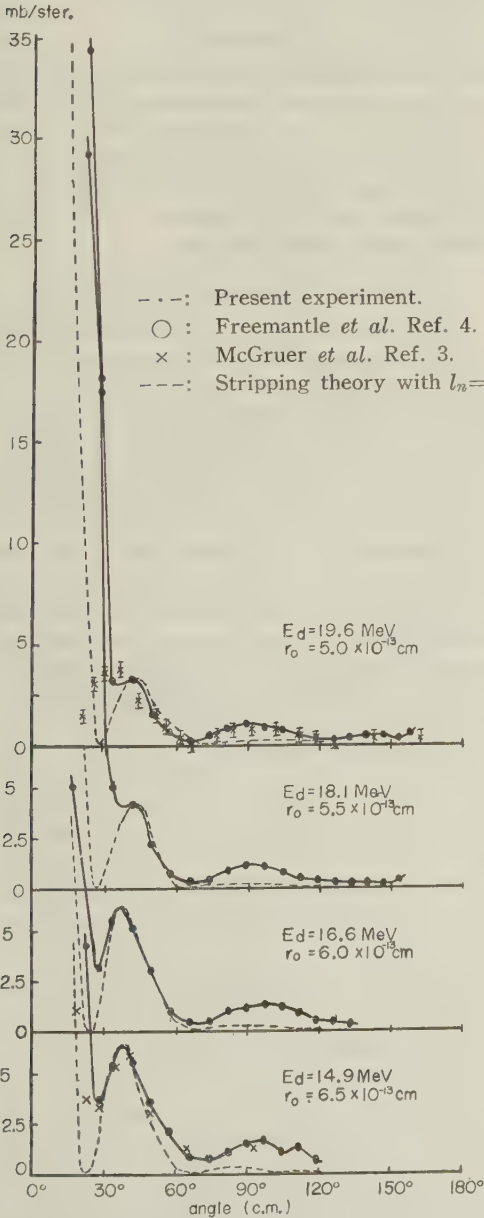


Fig. 5. Angular distributions of protons from the $C^{12}(d, p)C^{13}$ 3.09-MeV state reaction.

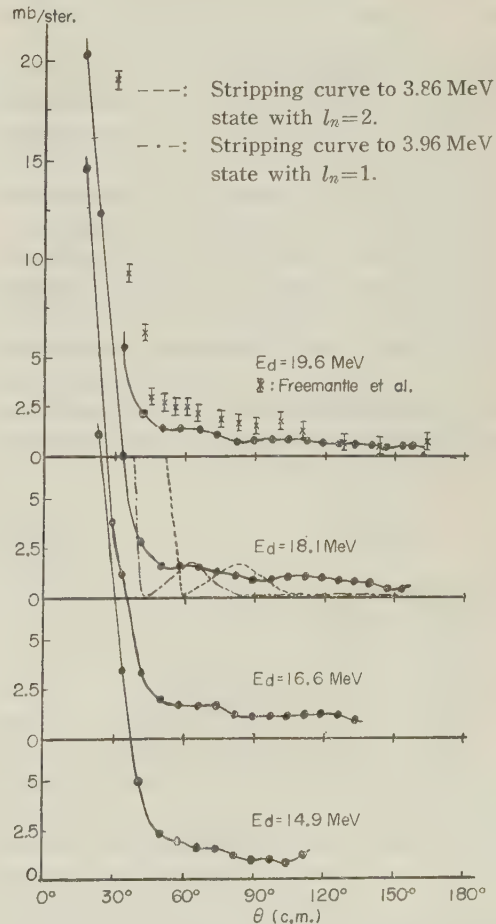


Fig. 6. Angular distributions of protons from the $C^{12}(d, p)C^{13}$ 3.69- and 3.86-MeV state reaction.

3.69- and 3.86-MeV levels, for the four values of deuteron energy.

As the spins and parities of the 3.69- and 3.86-MeV states of C^{13} have been found to be $3/2^-$ and $5/2^+$, respectively, it is expected that the stripping transitions with $l_n=1$ and $l_n=2$, respectively to these states, will be predominant. The theoretical angular distributions for these transitions were calculated with $r_0=5.6 \times 10^{-13}$ cm only for the deuteron energy of 18.1 MeV, because of the small change of theoretical angular distribution with the deuteron energy, and are shown in Fig. 6 with the arbitrary scales for their ordinates. It may be concluded from this figure that the transition to the 3.69 MeV state with $l_n=1$ is more predominant than that to the 3.86 MeV state with $l_n=2$. But the results obtained by McGruer *et al.* show the cross section for the 3.86 MeV state larger by one order of magnitude than that for the 3.69 MeV state in the extreme forward direction, and the theoretical curve with larger value of $r_0=7.0 \times 10^{-13}$ cm, for the 3.86 MeV state group can be fitted to the observed distribution. The angular distributions of these two proton groups, resolved separately, are necessary to obtain a definite conclusion. Although McGruer *et al.*³⁾ resolved these proton groups with a magnetic analyser and measured the angular distributions, they did not obtain the absolute value of the cross section and the measurements were confined only in small angular ranges in the forward directions. The experimental distribution, obtained by Freemantle *et al.*⁴⁾

at $E_d=19.0$ MeV and shown in Fig. 6, is also that for the unresolved proton groups to the 3.69- and 3.86-MeV states and the general behavior is quite consistent with the present data, but their absolute cross sections are somewhat larger than the present result.

The authors express their cordial thanks to Prof. I. Nonaka for his support and discussions throughout this work and to the cyclotron crew of I.N.S. of University of Tokyo for their operations of the cyclotron.

References

- 1) M. T. McEllistrem, K. W. Jones, R. Chiba, R. A. Donlas, D. F. Herring and E. A. Silverstein: Phys. Rev. **104** (1956) 1008. T. W. Bonner, J. T. Eisinger, A. A. Kraus, Jr. and J. B. Marion: Phys. Rev. **101** (1956) 209.
- 2) S. Green and R. Middleton: Proc. Phys. Soc. London **69A** (1956) 28.
- 3) J. N. McGruer, E. K. Warburton and R. S. Bender: Phys. Rev. **100** (1955) 235.
- 4) R. G. Freemantle, W. M. Gibson and J. Rotblat: Phil. Mag. **45** (1954) 1200.
- 5) A. E. Conzett, and D. G. Hoffman: Bull. Amer. Phys. Soc. **2** (1957) 382.
- 6) S. T. Butler, N. Austern and C. Pearson: Phys. Rev. **112** (1958) 1227.
- 7) I. Nonaka *et al.*: J. Phys. Soc. Japan **14** (1959) 1260.
- 8) R. Mather and E. Segré: Phys. Rev. **84** (1951) 191.
- 9) F. Ajzenberg and T. Lauritsen: Nuclear Phys. **11** (1959) 1.
- 10) A. B. Bhatia, K. Haug, R. Huby and H. O. News: Phil. Mag. **43** (1952) 1766.

Elastic and Inelastic Scattering of 11.2 MeV Deuterons

By Minoru TAKEDA

Department of Physics, Faculty of Science, Osaka University, Osaka

(Received November, 4, 1959)

The differential cross section for deuteron-nucleus elastic scattering has been measured for N, O, Ne, Mg, Al, S, A, Ca, Cr, Fe, Ni, Cu, Kr, Ag, Xe and Au at the deuteron energy of 11.2 MeV. Measurements were done at 5° intervals from 15° to 165° with relative uncertainty of 3 to 5%. Deuterons were detected by a thin CsI(Tl) crystal whose energy resolution was about 4% so that in almost all the cases inelastic deuterons and protons produced from (d, p) reaction were rejected. The measured cross sections show a pronounced diffraction pattern in light and medium weight nuclei. But the cross sections for heavier elements show a smooth decrease and are smaller than the Rutherford cross sections.

The cross sections of deuterons leading to the first excited state of ^{20}Ne and ^{24}Mg by inelastic scattering have been obtained. However, we could not detect inelastically scattered deuterons in other elements. The angular distributions for ^{20}Ne and ^{24}Mg are explained by the direct nuclear process.

§ 1. Introduction

The elastic scattering of protons¹⁾, neutrons²⁾ and alpha particles³⁾ by various nuclei has been studied over a wide range of incident energies by a number of investigators. These measurements show that the cross section for the elastic scattering of protons¹⁾ usually remains in the same order of magnitude as Rutherford scattering, and the cross section for alpha particles³⁾ shows a much stronger decrease with increasing angle. These results have been found to be generally consistent with the prediction of the optical model⁴⁾. Since the deuteron is a loosely bound and spin one particle, it is of interest to see whether the elastic scattering of deuterons can be considered in the same ways as those of protons, neutrons and alpha particles. However, there have been rather few systematic measurements of the elastic scattering of deuterons⁵⁾. Gove has reported on the elastic scattering of 15.2 MeV deuterons and Rees and Sampson have measured the differential cross section at 11 MeV for some heavy elements. These angular distributions show no diffraction pattern. Nishida⁶⁾ has fitted the data assuming that the electric break-up of the deuteron is the main contribution. The elastic cross sections for light nuclei exhibit an oscillatory behavior. Yntema has measured the angular distributions for a number

of medium and heavy elements at 21.6 MeV which show pronounced diffraction patterns. Measurements at 3.32 MeV and 4.07 MeV have been reported by Slous and Alford on nine elements and the analysis have been done. All these results may be explained by the optical model. Melkanoff⁷⁾ showed that the 13.5 MeV and 15 MeV data were explained by the diffuse surface optical model analysis.

Recently, considerably large polarizations of elastically scattered protons were observed and it was proved that the spin orbit coupling was contained in the proton-nucleus interaction besides the usual central optical potential⁸⁾. This suggests the presence of spin orbit interaction in the deuteron-nucleus scattering.

The present measurements were intended as a survey of elastic deuteron scattering over a wide range of elements from nitrogen to gold at approximately 11 MeV to search these features described above. In order to determine the optical model parameter, it may be desirable to cover the range of atomic numbers as wide as possible and also to provide sets of neighboring elements to facilitate the detection of possible effects due to nuclear spin, shape and shell structure.

There are a few reports on the inelastic deuteron scattering⁹⁾. Haffner observed diffraction pattern in some light elements. His

results show a forward peak in all the cases, while in many other measurements any forward peak does not appear. We have measured the differential cross sections of inelastic deuteron scattering for neon and magnesium which have relatively large differential cross sections, in order to study the direct interaction features in the reaction.

§ 2. Experimental Procedure

The Osaka University Cyclotron was used to produce a 11.2 MeV deuteron beam. The layout of the cyclotron and associated equipments have been shown elsewhere¹⁰⁾. This experiment was performed in a scattering chamber of 51 cm in diameter. The angular position of the counter could be measured to $\pm 0.1^\circ$. The angular resolution was $\pm 0.1^\circ$. The data was taken from 15° to 165° with an interval of 5° . The beam was collected in a Faraday cup which was always held at ground potential. The collector cup was connected to a vibrating reed electrometer and a condenser.

A CsI(Tl) crystal combined with a RCA 6342 photomultiplier was used to detect the scattered deuterons. Signals were amplified with a conventional fast amplifier and analyzed with a 20-channel pulse height analyzer. There are a great number of protons produced by the (d, p) reaction which have nearly the same energy as the elastically scattered deuterons. Moreover, there exist positive Q -value (d, α) reactions, though their cross sections have quite small values. Therefore, it is necessary to separate these particles. We made use of the fact that the range of an 11 MeV deuteron is quite larger than that of an alpha particle produced by (d, α) reaction and considerably less than that of a proton with the same energy. We used a CsI crystal with uniform thickness of 150 mg/cm^2 which corresponded to the range of a 9 MeV deuteron or a 7 MeV proton. An aluminum absorber was always inserted to stop the alpha particles and its thickness was increased until the pulse height of the elastic deuteron peak reached a maximum at each angular position. To minimize the effect of the multiple scattering in the absorber, we mounted the crystal close to the absorber. The scintillation crystal was considerably larger than the dimensions of slit. The arrangement is shown in Fig. 1.

In the measurement of inelastic scattering we used the following method, in the forward angle, to reduce the background due to the large elastic tail. We reduced aluminum absorber until the range of inelastically scattered deuterons which corresponded to the first excited level of target nuclei became equal to the crystal thickness. In this case the largest pulse height was obtained for the inelastically scattered deuteron corresponding to the first excited level and the elastic pulse height was smaller and broader than the inelastic peak. Typical pulse height spectra,

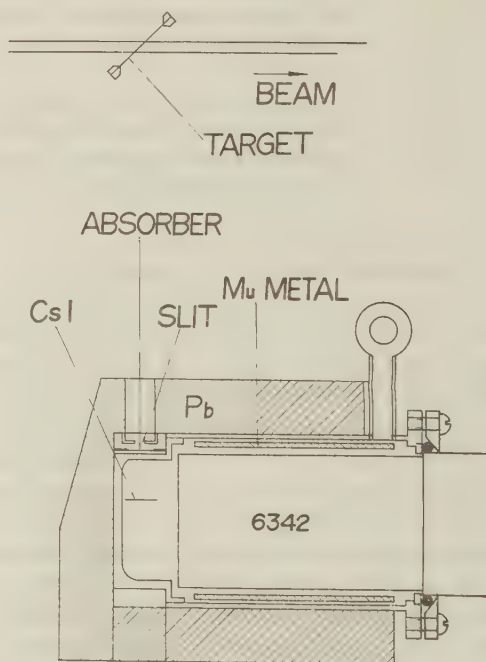


Fig. 1. The layout of detector system.

obtained for magnesium at 50° and 30° and for gold at 70° , are shown in Fig. 2. It is shown that the elastically scattered deuterons are completely separated from the inelastically scattered ones and the protons of various energy. The energy resolution of the detector was about 4%. The inelastic peak was not separated from continuous proton background, so the error of inelastic scattering cross section was quite large because of subtraction ambiguity.

Both metallic foils and gases were used in this experiment as the targets. They were chosen to cover the wide range from low to high atomic number. The foil targets were a few mg/cm^2 in thickness which were pre-

pared by evaporation or made from commercially available foils of natural isotopic abundances, and were placed at 45° to the beam direction. The thickness of these foils were assumed to be uniform within several percents. Copper and silver foils were 9 and 6 mg/cm^2 respectively, so that the mean incident energies at the centres of targets were somewhat less than those in other cases. We could not find any oxygen or other contaminations in the pulse height distributions. The gases were filled in the gas target cell with a 15μ aluminum window to about $1/3$ atoms, therefore the incident energy in the center of the target cell was somewhat less than that in the case of foil target. All the target gases were pure simple substances except sulphur. We used SH_2 gas as sulphur target because there was no disturbance from the hydrogen except in the region of small angle.

The SH_2 gas was purified by a liquid air trap.

There were some sources of errors. Especially at very small angles, the angles, the error due to the angular uncertainty was somewhat large. The disturbances to the elastic cross sections by inelastic scattering groups could be neglected for the elements lighter than nickel, but it was not clear for the elements heavier than copper. It was considered that the disturbance might be small. For the elements lighter than neon, the error due to the background subtraction was large at backward angles. For all the elements except nitrogen, oxygen and neon, the relative accuracy of the measurement was estimated to be about 3% for elastic scattering. For nitrogen, oxygen and neon the relative error was about 5%. The absolute error was believed to be about 10%. Inelastic peaks could not be separated from the continuous background of protons from (d, p) reactions, so the error of inelastic cross section was quite large because of the ambiguity in background subtraction. The relative error of inelastic scattering cross section was about 10%.

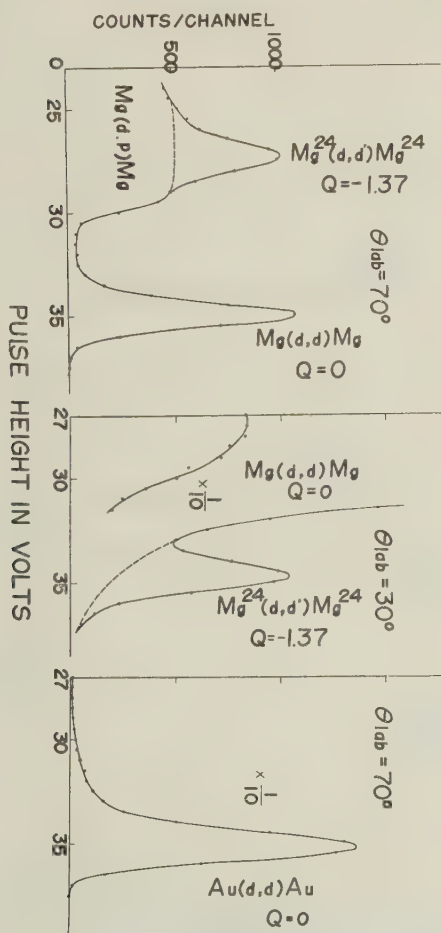


Fig. 2. The pulse height spectra for magnesium at 50° and 30° and for gold at 70° .

§ 3. Results and Discussion

The experimental results obtained for the elastic scattering are shown in Figs. 3 to 18. Also the Rutherford cross sections are shown with dotted curves in these figures. The corrections due to the finite size of target and detector slit and the multiple scattering of incident deuterons in the target are estimated to be negligible even for the extremely forward angle.

Nitrogen and oxygen have almost the same values of nuclear mass and their angular distributions are similar in spite of their different nuclear spin as is shown in Figs. 3 and 4, and an appreciable differences in the shapes of the distributions are observed in backward angles. The angular distributions for magnesium and aluminum are also similar in this respect as is shown in Figs. 6 and 7. Argon and calcium nuclei have been identical mass number and their cross sections have nearly the same angular dependences, although they differ by a factor of nearly two at some points, as is shown in Figs. 9 and 10. Although nickel and copper nuclei have different spins, we cannot find any special difference

in the angular distribution.

The characteristic features of these angular distributions are in their smooth variation of the positions of maxima and minima and of relative amplitude of diffraction pattern with atomic number. The amplitude decreases as the atomic number increases and the diffraction pattern vanishes completely in silver. The cross sections are always smaller than

those of Rutherford scattering except in the cases of nitrogen and oxygen whose cross sections exceed those of Rutherford at oscillation maxima and also in backward angles. Although we studied many elements having

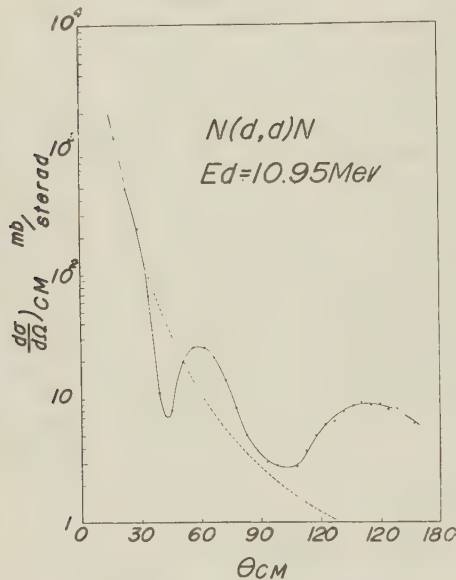


Fig. 3. The solid curve is the experimental angular distribution of elastically scattered deuteron from nitrogen. The dashed curve is the Rutherford cross section.

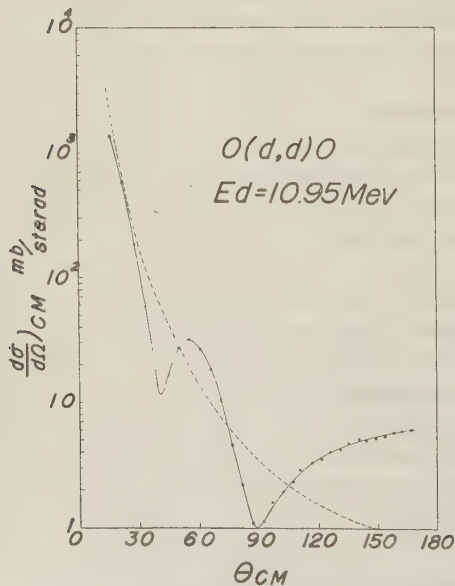


Fig. 4. Differential cross section for oxygen.

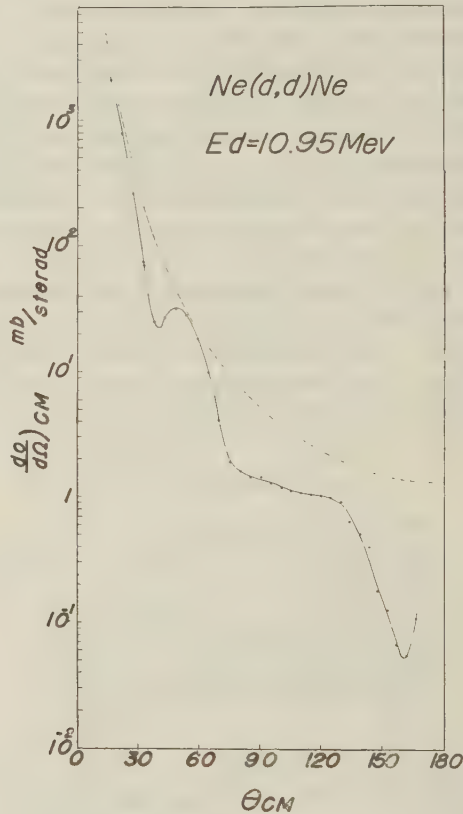


Fig. 5. Differential cross section for neon.

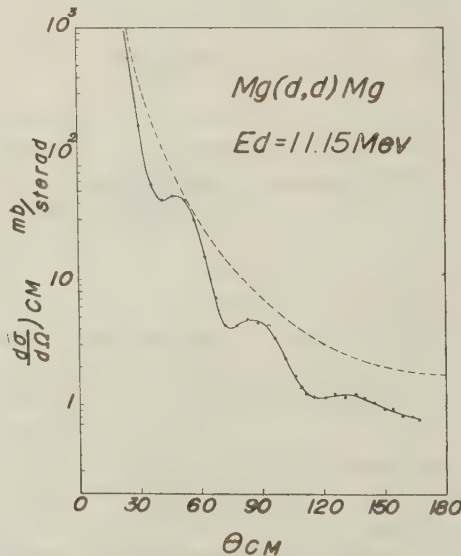


Fig. 6. Differential cross section for magnesium.

different nuclear spins, we could not observe any appreciable effect of the spin on the elastic angular distribution.

The simple theory for the diffraction of a plane wave by a completely absorbing sphere of radius R leads to the expression¹¹⁾

$$\frac{d\sigma}{d\Omega} = k^2 R^4 \left[\frac{J_1\left(2kR \sin \frac{\theta}{2}\right)}{2kR \sin \frac{\theta}{2}} \right]^2.$$

This expression is valid only for small angles. For a given feature of the diffraction pattern

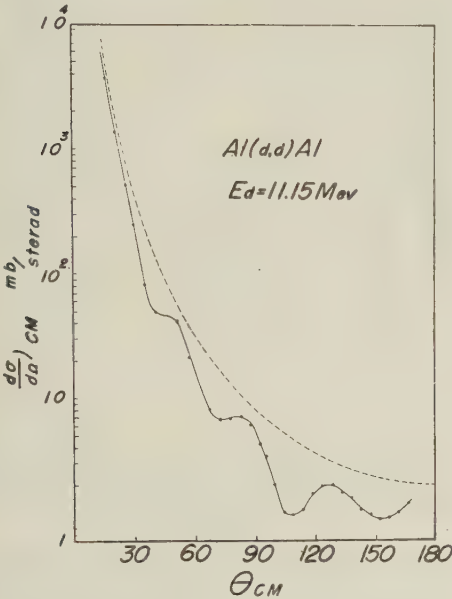


Fig. 7. Differential cross section for aluminum.

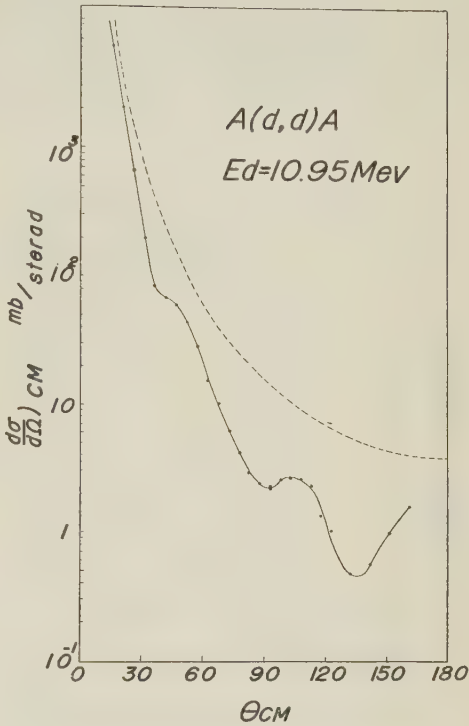


Fig. 9. Differential cross section for argon.

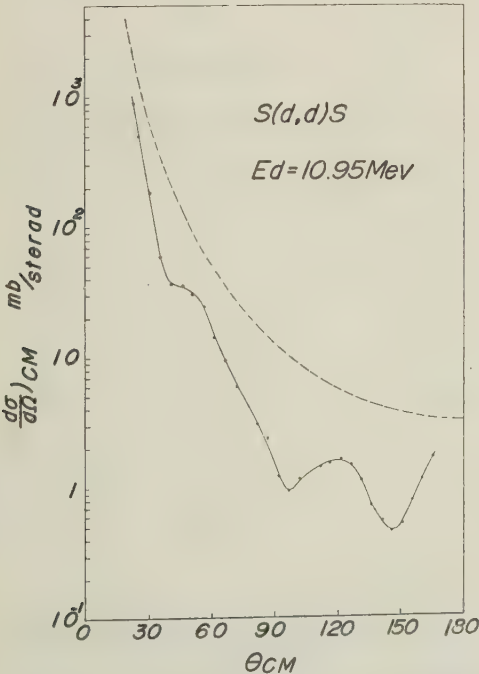


Fig. 8. Differential cross section for sulphur.

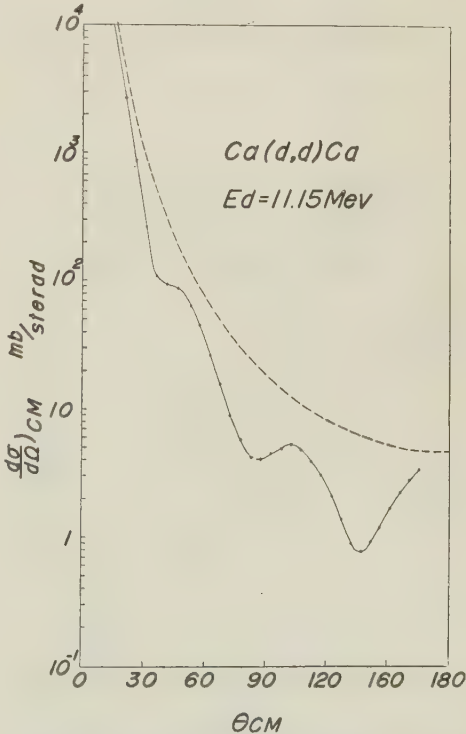


Fig. 10. Differential cross section for calcium.

(e.g., maxima or minima), one would expect $kR \sin(\theta/2)$ to remain approximately constant as R is varied. Fig. 19 shows the variation in the locations of the maxima and minima in the differential cross sections. It is interesting that the second minimum and the third

maximum vanish in the nuclei heavier than aluminum. Moreover, it is quite strange that

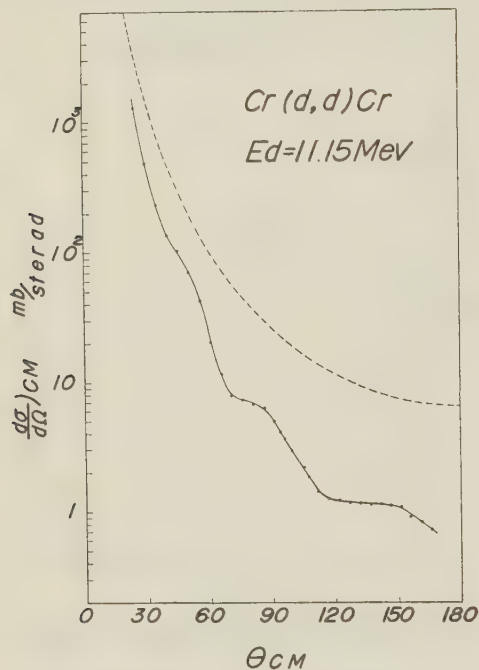


Fig. 11. Differential cross section for chromium.

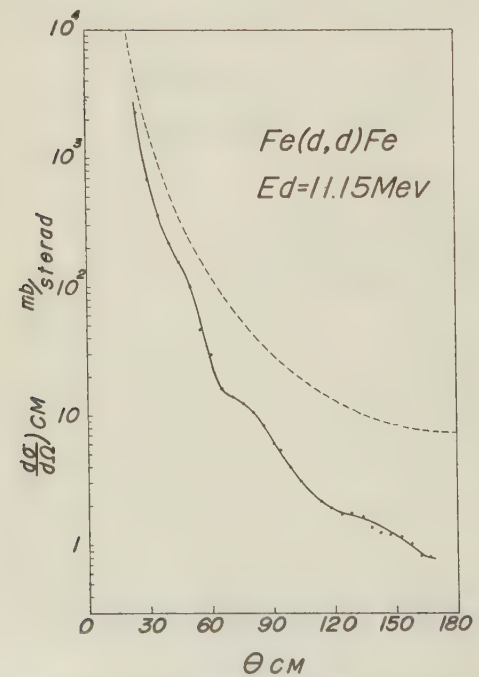


Fig. 12. Differential cross section for iron.

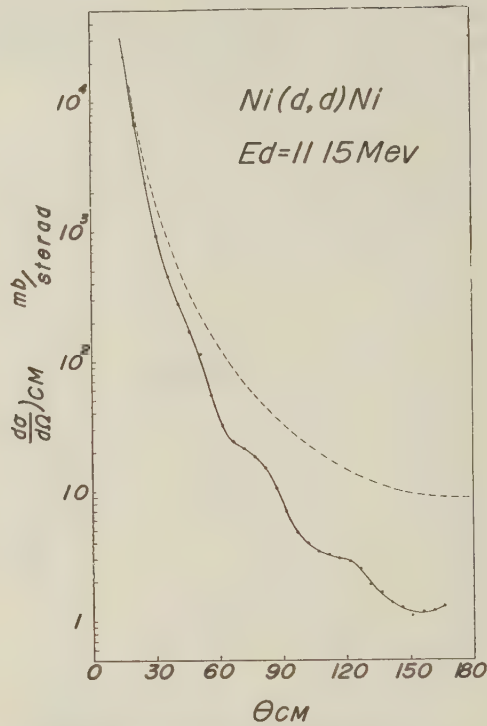


Fig. 13. Differential cross section for nickel.

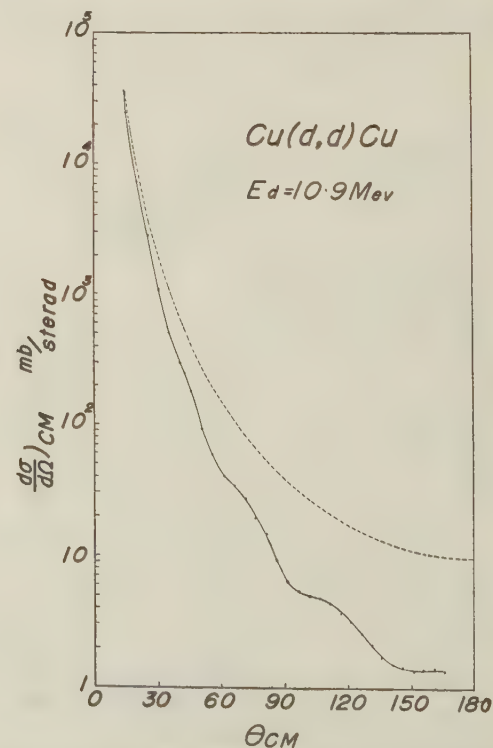


Fig. 14. Differential cross section for copper.

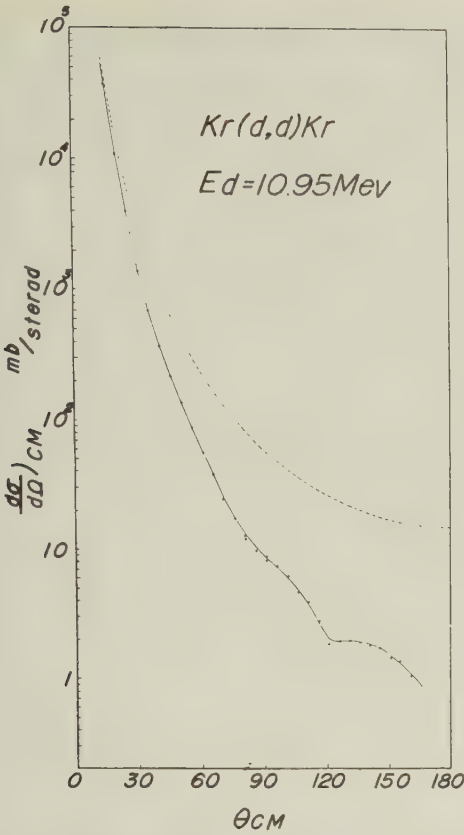


Fig. 15. Differential cross section for krypton.

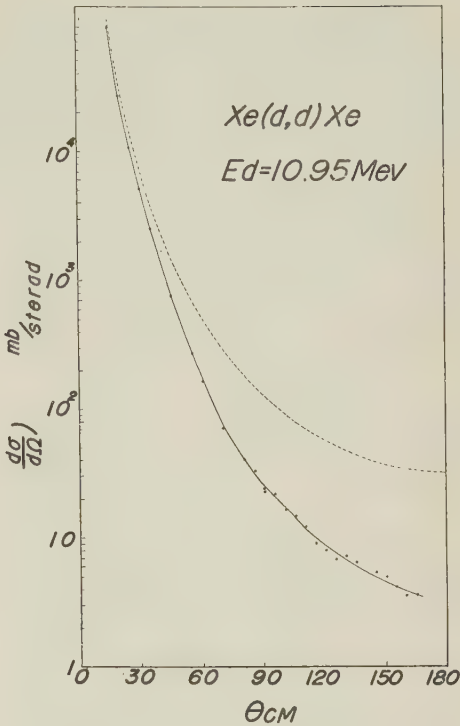


Fig. 17. Differential cross section for xenon.

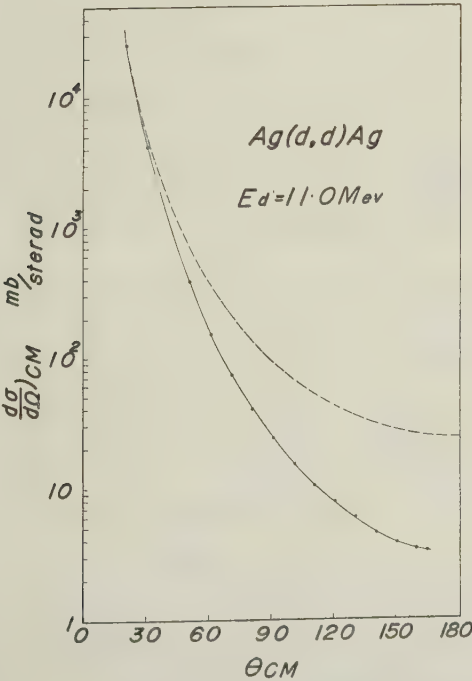


Fig. 16. Differential cross section for silver.

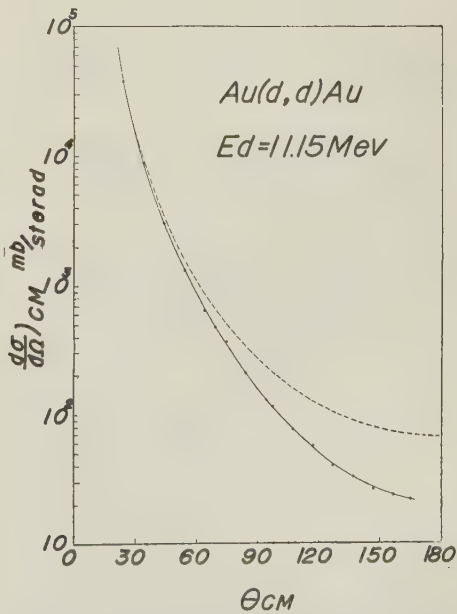


Fig. 18. Differential cross section for gold.

the first minimum does not change its position for almost all the elements.

On the other hand, the differential cross sections of 9.8 MeV and 17 MeV protons¹¹ show that there are some regularities in the locations of the maxima and minima. That is, the points plotted on the $1/R-\theta$ plane which represent the positions of minima of each order, lie on a straight line.

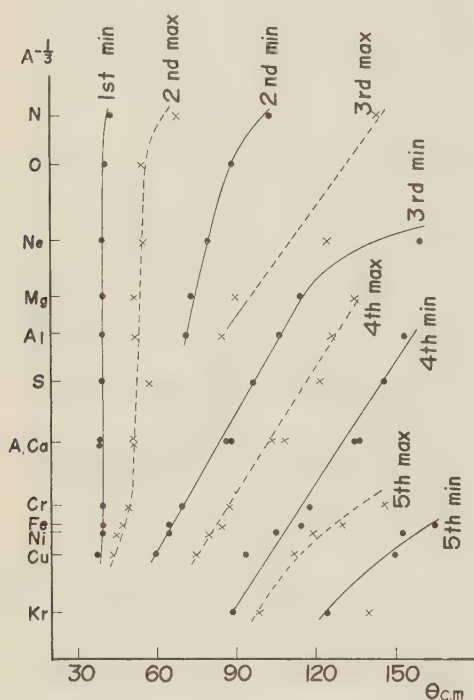


Fig. 19. Locations of the minima and maxima in the scattering cross sections as functions of nuclear radius.

Though it is not clear that the optical model is applicable to the elastic scattering of deuterons, there have been some successes in optical model analysis. In the previous paragraph, we pointed out that Melkanoff⁽⁷⁾ and Slaus⁽⁵⁾ explained the experimental results for the elastic scattering of deuterons by using the optical model analysis. Another success was obtained in the (d, p) stripping reaction. That is, Tobocman, by using the wave functions distorted by the optical potential, obtained the theoretical curves of angular distributions more fittable than those obtained from simple Butler theory¹⁶⁾. There does not appear any polarization of emerging protons in the theory using the plane wave approximation, and Tobocman explained the experimental

results on polarization by using the distorted wave method. The incident deuteron wave and the outgoing proton wave were distorted by the nuclear optical potential. It may seem to be strange that the optical model is successful in the elastic scattering of deuterons. Therefore, it is necessary to study in detail why this treatment is applicable to such loosely bound composite particles as deuterons. Recently Sano proved theoretically that the optical model is applicable to the elastic scattering of deuterons as the first approximation¹²⁾. He fitted the main feature of our magnesium data with a theoretical result using reasonable parameters of square well optical model. The usual Wood-Saxon potential may explain more closely these data, so it is desirable to determine many parameters of this potential. Since the spin orbit interaction is necessary in the elastic proton scattering to fit both the angular distribution and the spin polarization, this interaction would also be necessary for the case of deuteron scattering. If the elastic deuteron scattering data are fitted well by a optical potential with spin orbit term, then the polarizations and the non-elastic cross sections of deuterons will also be predicted. The compound elastic scattering is assumed to have negligible contri-

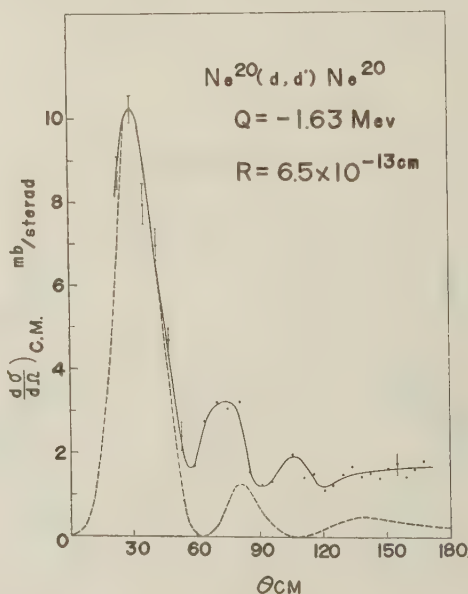


Fig. 20. The solid curve is the experimental angular distribution of inelastically scattered deuterons from the 1.63 MeV level of Ne^{20} . The dashed curve is the theoretical cross section predicted by Huby and Newns.

bution to the elastic cross section for our case.

The differential cross sections for inelastically scattered deuterons by magnesium and neon to the first excited states are illustrated in Figs. 20 and 21. Many theories of inelastic deuteron scattering were proposed up to now¹³⁾ and some of these were based on collective excitation. In the present paper we have explained these inelastic cross sections from a single particle aspect. The dotted curves shown in these figures represent the attempts to fit these data with a direct interaction model by Huby and Newns¹⁴⁾. The characteristic features are rather well reproduced

gestions and for many discussions. Above all, the author wants to thank Messrs. C. Hu and S. Kato who gave him help, advice and encouragement throughout the course of the experiment.

References

- 1) B. L. Cohen and R. V. Neidigh: Phys. Rev. **93** (1954) 282. I. E. Dayton and G. Schrank: Phys. Rev. **101** (1956) 1358. D. A. Bromley and N. S. Wall: Phys. Rev. **102** (1956) 1560. B. B. Kinsey and T. Stone: Phys. Rev. **103** (1956) 975. N. M. Hintz: Phys. Rev. **106** (1957) 1201. C. A. Preskitt and W. P. Alford: Atomic Energy Commission Report NYO-2172. M. K. Brussel and J. H. Williams: Phys. Rev. **114** (1959) 525.
- 2) M. Walt and J. R. Beyster: Phys. Rev. **98** (1955) 677. R. C. Allen, et al.: Phys. Rev. **104** (1956) 731. J. R. Beyster, et al.: Phys. Rev. **104** (1956) 1319. J. D. Anderson, et al.: Phys. Rev. **110** (1958) 160.
- 3) R. E. Ellis and L. Schecter: Phys. Rev. **101** (1956) 636. G. W. Farwell and H. E. Wegner: Phys. Rev. **95** (1954) 1212. E. Bleuler and D. J. Tendam: Phys. Rev. **99** (1955) 1605. G. Igo, et al.: Phys. Rev. **101** (1956) 1508.
- 4) G. Igo and R. M. Thaler: Phys. Rev. **106** (1957) 126. M. A. Melkanoff, et al.: Phys. Rev. **106** (1957) 793. A. E. Glassgold, et al.: Phys. Rev. **106** (1952) 1207. W. B. Cheston and A. E. Glassgold: Phys. Rev. **106** (1957) 1215. A. E. Glassgold and P. J. Kollogg: Phys. Rev. **106** (1957) 1372. F. E. Bjorklund and S. Fernbach: Phys. Rev. **109** (1958) 1295.
- 5) W. M. Gibson and E. E. Thomas: Proc. Roy. Soc. A, **210** (1952) 543. G. W. Greenless: Proc. Phys. Soc. London A, **68** (1955) 97. H. E. Gove: Phys. Rev. **99** (1955) 1353. J. R. Rees and M. B. Sampson: Phys. Rev. **108** (1957) 1289. G. R. Summers-Gill: Phys. Rev. **109** (1958) 1591. J. L. Yntema: Phys. Rev. **113** (1959) 261. I. Slaus and W. P. Alford: Phys. Rev. **114** (1959) 1054. C. E. Porter: Phys. Rev. **112** (1958) 1722.
- 6) Y. Nishida: Progr. Theor. Phys. **19** (1958) 389.
- 7) H. S. Melkanoff: Tue Florida Conference on the nuclear optical model (1959) 207.
- 8) L. Rosen and J. E. Brolley: Phys. Rev. **107** (1957) 1454. K. W. Brockman: Phys. Rev. **110** (1958) 163. L. Rosen and J. E. Brolley: Geneva Conference (1958). W. A. Blanpied: Phys. Rev. **113** (1959) 1099. R. E. Warner and W. P. Alford: Phys. Rev. **114** (1959) 1338.

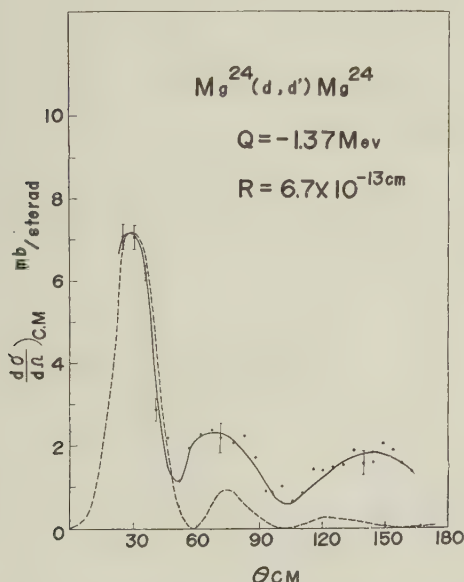


Fig. 21. The experimental and the theoretical angular distributions of inelastically scattered deuterons from the 1.37 MeV level of Mg^{24} .

with reasonable interaction radii. The absolute values of the cross sections are rather small compared with those of proton scattering of the same energy leading to the same levels. We could not find any inelastically scattered deuteron groups in medium and heavy nuclei, though Yntema¹⁵⁾ has reported such deuteron groups with a considerably large cross section.

Acknowledgement

The author is very grateful to Professor T. Wakatsuki for giving him the opportunity to carry out this investigation, and for his constant interest. I am indebted to Dr. M. Sano and T. Kammuri for their valuable sug-

- 9) W. F. Vogelsang and J. N. McGruer: Phys. Rev. **109** (1958) 1663. M. B. Sampson: Phys. Rev. **108** (1957) 1289. J. W. Haffner: Phys. Rev. **103** (1956) 1398. J. L. Yntema and B. Zeidman: Phys. Rev. **114** (1959) 815.
- 10) M. Takeda, et al.: J. Phys. Soc. Japan **12** (1957) 561. Y. Oda, et al.: J. Phys. Soc. Japan **14** (1959) 396.
- 11) L. W. Seenson, U. Schindewolf and N. S. Wall: Nucl. Phys. **6** (1958) 203.
- 12) M. Sano: Private communication.
- 13) W. J. Fairbairn: Proc. Roy. Soc. A, **238** (1957) 448. S. T. Butler: Phys. Rev. **106** (1957) 272. J. Sawichi: Nucl. Phys. **6** (1958) 613. El Nadi: Soviet Phys. **7** (1958) 834. J. S. Blair: Phys. Rev. **115** (1959) 928.
- 14) R. Huby and H. C. Newns: Phil. Mag. **42** (1951) 1442.
- 15) J. L. Yntema and B. Zeidman: Phys. Rev. **114** (1959) 815.
- 16) W. Tobocman: The Florida Conference on the Nuclear Optical Model. (1959) 123.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

On the Phase Transition of Tungsten Trioxide below Room Temperature

By Sigetosi TANISAKI

Faculty of Literature and Science, Yamaguchi University

(Received November 27, 1959)

Microscopic observation, thermal analysis, measurement of electrical resistivity and X-ray study of WO_3 were carried out in relation to the phase transition from room temperature down to -70°C . The crystal of WO_3 is monoclinic ($a=7.30\text{\AA}$, $b=7.53\text{\AA}$, $c=7.68\text{\AA}$, $\beta=90^\circ54'$) at room temperature, and it transforms to triclinic ($a=7.30\text{\AA}$, $b=7.52\text{\AA}$, $c=7.69\text{\AA}$, $\alpha=88^\circ50'$, $\beta=90^\circ55'$, $\gamma=90^\circ56'$) near 17°C , and transforms to monoclinic ($a=5.27\text{\AA}$, $b=5.16\text{\AA}$, $c=7.67\text{\AA}$, $\beta=91^\circ43'$) near -40°C , on cooling. These two transitions could be clearly observed in the single-domain crystal in the room temperature phase, but the phase transitions of complicated appearance were observed in the multidomain crystal owing to a small difference between free energies in the room-temperature phase and the triclinic phase. Both electrical resistivity versus temperature curve and thermal differential curve show a slight anomaly at 17°C transition and a remarkable anomaly at -40°C transition.

§ 1. Introduction

Concerning to the ferroelectricity or antiferroelectricity of WO_3 many investigations have been performed.¹⁻⁴⁾ Above room temperature WO_3 has very high dielectric constant, and many phase transitions have been reported. It has a monoclinic lattice at room temperature and transforms to an orthorhombic one at 350°C and to a tetragonal one at 740°C . Two more phase transitions at 950°C and 1250°C have been known, but the crystal is remained to be tetragonal up to 1350°C and a transition to cubic phase has not been known. Each phase has lower symmetry variations of the cubic structure of ReO_3 type. Though

these facts suggest the possibility of ferroelectricity or antiferroelectricity above room temperature, it has not been ascertained owing to its high electrical conductivity.

On the other hand, below room temperature a phase transition at about -50°C has been reported.^{2), 5), 6)} Matthias and Wood²⁾ succeeded to observe a hysteresis loop at -198°C without interference of dielectric loss, and then WO_3 has been thought to be ferroelectric in the low temperature phase. There are several points left to be studied about the phase transition of this material below room temperature. Hirakawa⁵⁾ observed a gradual and complicated change of domain structure

in the wide temperature range from -50°C to room temperature, but the reason of such complicated change has not been clear. According to the dilatometric measurements of Hirakawa⁵⁾ or other investigators,^{3), 6)} a remarkable contraction was observed near -50°C , and yet Sawada³⁾ could not observe any noticeable specific heat anomaly, corresponding to such a remarkable volume change but observed a slight anomaly whose amount was only a little larger than experimental error. The low temperature phase has been supposed to be trigonal from the facts that the symmetrical extinction was observed if viewed along c axis by polarizing microscope⁵⁾ and a higher crystal symmetry was reported from X-ray study,²⁾ but the supposition is not based on any conclusive evidence. Further, recently Sawada and Danielson⁷⁾ studied the electrical conduction of single crystal from room temperature to 1000°C , but below room temperature the conductivity has not been measured. Concerning to these points, optical, thermal, electrical, and X-ray studies of this material have been carried out in this work.

§ 2. Preparation of Samples

Single crystals of WO_3 were prepared by the sublimation method previously reported.⁸⁾ The plate crystals having c axis perpendicular to the plane of plate (c crystal) and an area of about $5 \times 5 \text{ mm}^2$ can be obtained by this method. The crystals usually have a domain structure with walls of (110) and (100) twin planes at room temperature, but they can be changed to single-domain crystals by the appropriate external stress as previously reported.⁹⁾ In many cases of the following study, single-domain crystals thus obtained were used. In the following, the words "single-domain crystal" and "multidomain crystal" mean the crystals of single domain and multidomain in the room temperature phase respectively.

§ 3. Optical Observation

When the c crystal of single domain was observed by the polarizing microscope with a simple low temperature stage, two crystallographic changes were found at about 17°C and -40°C on cooling (Photo. 1). Below 17°C the crystal has the domain structure

whose walls are (010) twin planes, and its colour changes from green to light green. The difference of extinction between two neighbouring domains is about 6° . When the crystal was viewed along a axis it was found that the difference of extinction between neighbouring domains is about 14° . The relations of extinction directions and crystal axes are shown in Fig. 1.

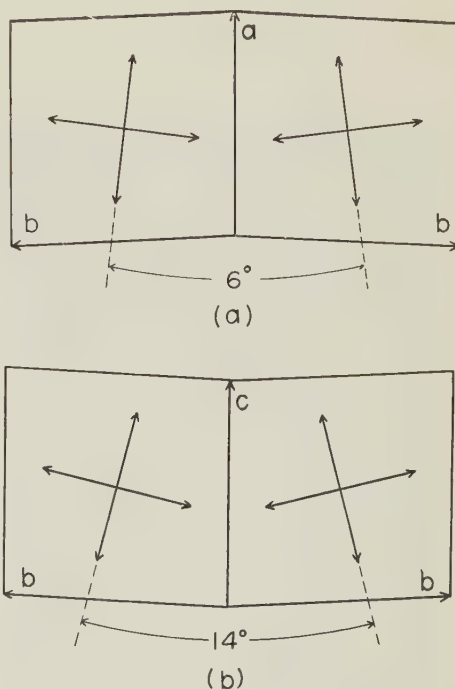


Fig. 1. Extinction positions of the neighbouring domains in the triclinic phase when viewed along (a) c axis and (b) a axis.

The second remarkable change occurs at about -40°C . The crystal becomes to be almost colourless and transparent and shows usually a very fine (010) twinning. This transition corresponds to -50°C transition reported by Matthias²⁾ and other workers.^{5), 6)} The extinction position rotates about an angle of 45° from that in higher temperature phase, and the symmetrical extinction was observed in the low temperature phase. This symmetrical extinction was one of the reasons that this low temperature phase had been supposed to be trigonal, but Iwai¹⁰⁾ pointed out first that if viewed along b axis extinction is not symmetrical but nearly parallel to a or c axis. It was confirmed again in our observation. It is evident from this optical

observation that the crystal is not trigonal.

The observed changes of the extinction position at the two transition points can be explained by the assumption for the changes of crystal symmetry, that at 17°C the monoclinic pseudocubic unit cell changes to triclinic pseudocubic by small shears in the (100) and (001) planes, and below -40°C a axis length becomes equal to b axis length and the new cell is monoclinic with its three axes in the directions $[1\bar{1}0]$, $[110]$ and $[001]$ relative to the pseudocubic cell. These as-

sumptions are supported by a X-ray investigation as described below in detail. In the following let us call these three phases, 350°C – 17°C , 17°C – -40°C and -40°C –, as the room temperature phase, the triclinic phase and the low temperature phase, respectively.

The two transitions near 17°C and -40°C can be clearly observed showing a thermal hysteresis in the single domain crystal, but the phase transitions of multidomain crystal are rather complicated. When the c crystal of multidomain is cooled down from room

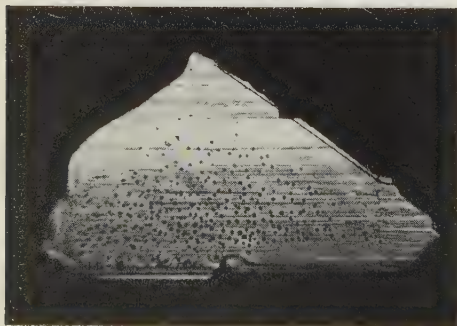
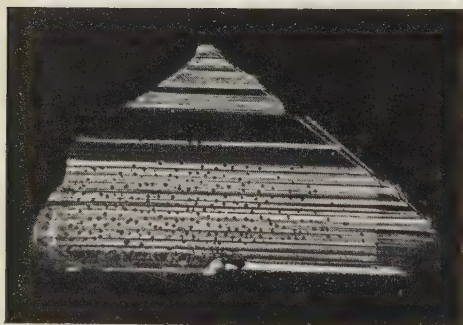
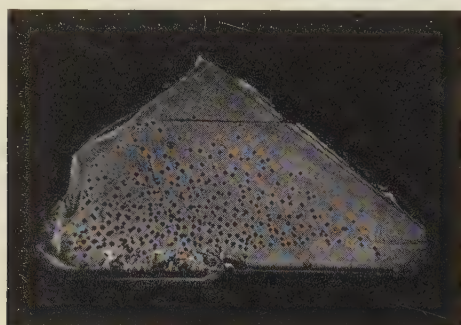


Photo. 1. Three phases of WO_3 observed between crossed nicols.

- (a) Room temperature phase (30°C). Only one (100) wall is seen near the right corner of the crystal.
- (b) Triclinic phase (10°C). The irregular boundary corresponding to the above (100) wall is seen.
- (c) Low temperature phase (-55°C).

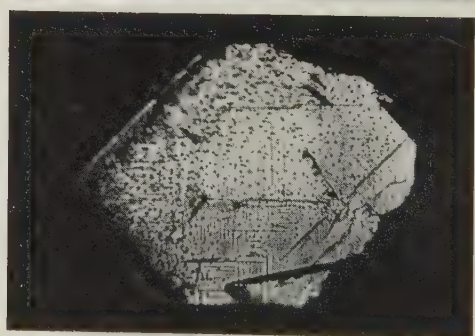
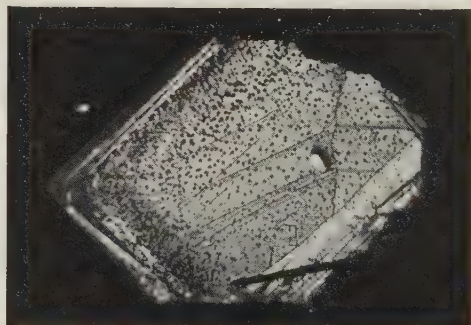
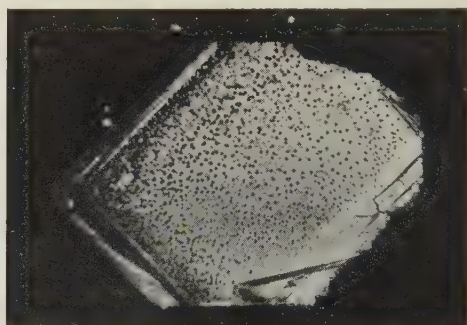


Photo. 2. Process of the phase transition in a multidomain crystal.

- (a) Room temperature phase (30°C).
- (b) Coexistence of the room temperature phase and the triclinic phase (-20°C).
- (c) Complicated domain structure of the low temperature phase (-50°C).

temperature, the triclinic phase frequently appears below 17°C at first at the edge of the crystal and grows step by step at the expense of its neighbouring domains with decreasing temperature, but often the growth of the triclinic phase seems to be hindered by (100) domain walls and then the (100) wall changes to a zigzag boundary between the triclinic part and the monoclinic part. Below 0°C a few narrow stripes with (100) domains of the triclinic phase, which run across the monoclinic part at an angle of about 60° with (100) wall, often appear in the interior part of *c* surface and grow in its length with decreasing temperature (Photo. 2(b), 3), and then a sudden change to the ordinary large triclinic part with (010) twins is sometimes observed. The crystal transforms to the low temperature phase near -40°C, and so the apparently direct transition from the room temperature phase to the low temperature phase is observed in some part of the crystal. Then obtained domain structure of low temperature phase is the complicated one. An example of such process is shown in Photo. 2.

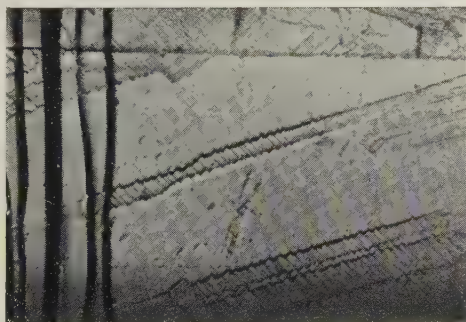


Photo. 3. Fine structure of triclinic stripes (-20°C).

When the crystal is heated up from the stage as shown in Photo. 2(b), triclinic stripes disappear even in the temperature below 0°C slowly with increasing temperature, but the large triclinic parts with (010) twins do not transform to the room temperature phase until the crystal is heated up to above 17°C. When the triclinic part with (010) twins transforms to the room temperature phase, we can hardly find (100) domain wall in that part and this part can easily transform at 17°C to triclinic on cooling.

The crystal in the low temperature phase

always transforms on heating to the triclinic phase near -25°C, and transforms to the room temperature phase rather gradually in a temperature range from 20°C to 30°C. After cooling and heating were repeated, the multidomain crystal usually breaks up into small pieces chiefly because of a remarkable volume change at -40°C transition, and each piece has a relatively simple domain structure and transforms to triclinic at 17°C on cooling without complexity.

On account of the complexity of the phase transition of multidomain crystal, the single-domain crystal must be used in many cases for the study of this material below room temperature.

§ 4. X-ray Investigation

In order to investigate the symmetry changes of WO_3 below room temperature, rotation- and oscillation-photographs of single-domain crystals, in which *a*, *b*, and *c* axes are vertical, were taken by using Nickel filtered $\text{CuK}\alpha$ radiation at about 30°C, 10°C, and -50°C. Obtained crystallographic data in each case are shown in Table I. The detailed analysis of the crystal structure of WO_3 in the room temperature phase will be reported in another paper.¹¹⁾

Table I. Crystallographic data of WO_3 .

1) Room temperature phase (at 30°C)
Monoclinic unit cell containing eight molecules:
$a=7.30\text{\AA}$, $b=7.53\text{\AA}$, $c=7.68\text{\AA}$, $\beta=90^\circ 54'$
2) Triclinic phase (at 10°C)
Triclinic unit cell containing eight molecules:
$a=7.30\text{\AA}$, $b=7.52\text{\AA}$, $c=7.69\text{\AA}$
$\alpha=88^\circ 50'$, $\beta=90^\circ 55'$, $\gamma=90^\circ 56'$
3) Low temperature phase (at -50°C)
Triclinic unit cell containing eight molecules:
$a'=7.38\text{\AA}$, $b'=7.38\text{\AA}$, $c'=7.67^\circ$
$\alpha'=88^\circ 48'$, $\beta'=91^\circ 12'$, $\gamma'=91^\circ 15'$
Monoclinic unit cell containing four molecules:
$a=5.27\text{\AA}$, $b=5.16\text{\AA}$, $c=7.67\text{\AA}$, $\beta=91^\circ 43'$

Among the lattice parameters of the triclinic phase at 10°C, the values of *a*, *b*, *c* and β are almost the same as those of the room temperature phase, and α and γ show slight deviations from 90°. The reflections in the first and third layer lines of rotation photo-

graphs for c vertical are very weak as in the room temperature phase. According to our preliminary analysis, the positions of tungsten atoms in the triclinic phase expected from Patterson projections along a and b axes are very similar to those in the room temperature phase. The detailed structure analysis is not easy owing to its triclinicity.

For the low temperature phase let us assume for convenience an unit cell with its three axes a' , b' and c' parallel to those of the triclinic phase and the room temperature phase, then a' axis length is equal to b' axis length but c' axis length is longer than those and so the low temperature phase can not be trigonal. For the confirmation of the relation $a' = b'$, reflections of (840) (480) and (820) (280) were taken on the same film, but any splitting of each spot could not be found. All of the observed reflections could be indexed by the monoclinic unit cell whose dimensions are shown in Table I. Of course it can not be determined only from this fact whether the low temperature phase has a monoclinic symmetry or a triclinic symmetry in which a' is equal to b' by chance. But taking into account the fact that by the microscopic observation the symmetrical extinction was found in this phase if viewed along c axis, it may be concluded that the low temperature phase has a true monoclinic symmetry. Fig. 2 shows the relation of triclinic axes and monoclinic axes in the low temperature phase.

The calculated unit cell volumes of each

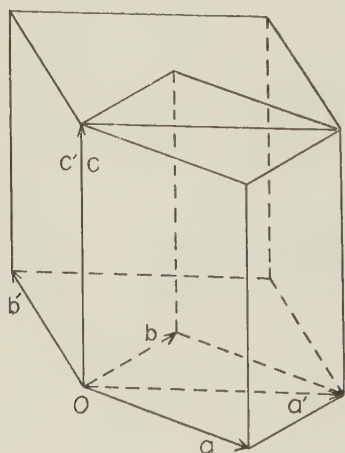


Fig. 2. Orientation of monoclinic axes (a, b, c) relative to triclinic axes (a', b', c') in the low temperature phase.

phase are $422.1\text{\AA}^3$ (30°C), $421.9\text{\AA}^3$ (10°C) and $417.5\text{\AA}^3$ (-50°C), in which the value of low temperature phase is the one for triclinic unit cell (a' , b' , and c'). These values suggest the remarkable volume contraction at -40°C transition. The volume difference between 30°C and -50°C estimated from the result of Hirakawa's dilatometry⁵⁾ is about a half of calculated value, but Sawada³⁾ obtained a larger volume change, exact value of which was not shown in his paper. The discrepancy of his value from X-ray data may be small.

§5. Thermal Properties and Complicated Phase Transition

The differential thermal analysis was performed from -60°C to 80°C in vacuum, and the heating rate was about $5^\circ\text{C}/\text{min.}$ About 1 cc of small crystals, each of which had a dimension of about 1mm^3 , were used for sample after the repeated heat treatments of heating and cooling between 50°C and -60°C in order to avoid the difficulty of the complicated phase transition near 17°C as much

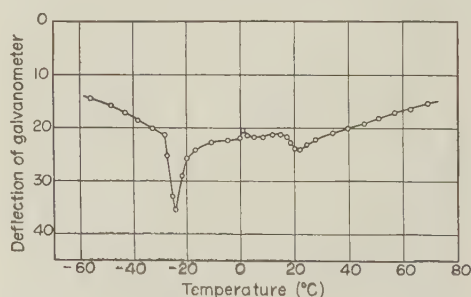


Fig. 3. Differential thermal curve of WO_3 .

as possible. Fig. 3 shows an obtained differential thermal curve, in which there are two endothermic peaks except an anomaly at 0°C caused by moisture of standard material (NaCl), a remarkable peak near -25°C and a small and broad peak near 20°C . The former certainly corresponds to the above described low temperature phase transition and the latter seems to correspond to the 17°C transition. Judging from the differential thermal curve, the specific heat anomaly at -40°C transition seems to be larger than that reported by Sawada.³⁾ A more accurate measurement of the specific heat is desirable. On the contrary the specific heat anomaly at 17°C transition may be relatively small. Then the difference between the free energy

of the room temperature phase and that of the triclinic phase is to be small and, as described below, the phase transition of multidomain crystal may be strongly affected by several factors. It seems that this is the reason of the complicated appearance of this phase transition.

Fig. 4 shows two possible ways of displacive transformation from the room temperature phase to the triclinic phase in which three axes hardly change in length, and in case (a) the transition takes place mainly by small shears in (100) and (001) and in another case (b) the shear in (010) is also necessary for the transition. It is reasonable to assume that the case (b) is more difficult to take place than the case (a). In fact, it was ascertained by X-ray method that only the transition of case (a) takes place reversibly by heating and cooling in the single-domain crystal. For the successive growth of the triclinic part without (100) domain wall in the multidomain crystal, it is necessary that

the transition proceeds at the expense of its neighbouring domains alternately in two ways (a) and (b), in which (b) is difficult to take place. This may be the reason why the transition does not proceed smoothly but the transition process is often hindered by (100) domain walls. If each (100) domain of multidomain crystal transforms to the triclinic phase with (010) twin in the way (a), it is evident from the lattice constants of the triclinic phase that the coherency is not satisfied at (100) domain wall. Then the strain energy is large, and such transition can hardly take place in multidomain crystal with fine (100) domains, but it was observed in the crystal with a few relatively large domains. If each (100) domain transforms to single domain of the triclinic phase, then (100) domains will be observed in the triclinic phase. But such transition was observed only in a few cases. This fact suggests that the wall energy of (100) domain may be larger than that of usually observed (010) domain in the triclinic phase. Further, when one part of the crystal of the room temperature phase transforms to triclinic, a certain stress distribution occurs around the triclinic part owing to the lattice deformation, and the strain energy in the crystal increases. But such stress distribution will be favourable to the transition to the triclinic phase in some part of the crystal. The stripes of the triclinic part in Photo. 2(b) and 3 might be due to such stress distribution. Of course the phase transitions may be also affected by the other factors beside these, for example, interfacial energy between two phases, residual internal stress, electrostatic energy if the crystal is polar and so on.

§ 6. Electrical Conductivity

The specific resistivity in the direction of a axis of single-domain crystals was measured from 100°C to -70°C. Measurements were performed in vacuum by the usual D. C. potentiometer method. Au was evaporated on the crystal as current electrodes and potential probes. Evaporated Au electrodes have usually a considerable contact resistance with sample and show the rectifying characteristic as well as the pressed platinum electrodes used by Sawada and Danielson.⁷⁾ Therefore when the voltage was reversed, the current

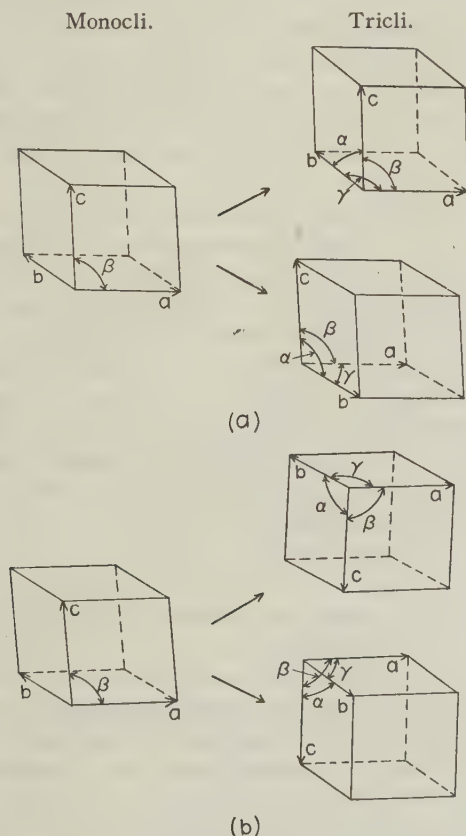


Fig. 4. Two possible ways of displacive transformation from the room temperature phase to the triclinic phase.

changed by several tens percent in some cases, but it was ascertained that the calculated resistance between potential probes was almost the same, and so measurements were performed in a definite direction of voltage. Applied voltage across the crystal was about 0.1 volt between 100°C and the lower transition point, and below it about 0.5 volt. Fig. 5 shows the specific resistance versus temperature curve of a crystal (breadth 1.18mm, thickness 0.31 mm, interval between potential probes 1.7 mm, length between current electrodes 4.4 mm). Above room temperature the specific resistance increases with increasing temperature in a similar way as was reported by Sawada and Danielson. But the absolute value at 30°C, 0.39 ohm cm for the above crystal, is slightly larger than their value. Below room temperature it shows two anomalies at about 17°C and -40°C on cooling. Below -40°C the specific resistance becomes more than ten times larger than that above this temperature. The steep increase below -40°C is not due to the gradual phase transition. It was ascertained by the microscopic observation that the transition of this crystal took place completely at about -40°C.

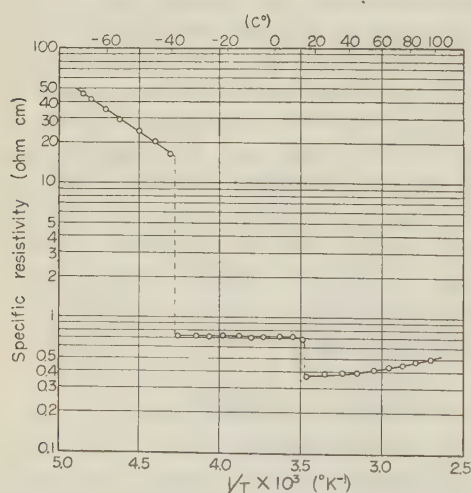


Fig. 5. Specific resistivity versus temperature curve of a single domain crystal.

Below -40°C WO_3 may be a typical impurity semiconductor.

Dielectric constant of the single crystal of WO_3 is very high (several thousands at 1 M.C.) at room temperature and suddenly decreases to several hundreds near -40°C.^{(12), (13)} If the dielectric property of WO_3 is closely

related to the electrical conductivity as pointed out by Sawada,⁽⁴⁾ the sudden change of both properties at -40°C transition is worthy to notice, and suggests a change of electronic structure. Concerning to this point, it is expected from the inspection of X-ray photographs that the crystal structure of the low temperature phase is considerably different from that of the room temperature phase and the triclinic phase. Especially reflections of the first and third layer lines of c vertical rotation photographs are fairly strong. This fact shows that tungsten atoms arranged parallel to c axis displace considerably in each other. A detailed structure analysis of the low temperature phase seems to be important as a basis of discussions about the dielectric and conductive properties of WO_3 .

§ 7. Summary

The following results were obtained from this study:

(1) WO_3 has a triclinic phase between the monoclinic phase above about 17°C and the low temperature phase below about -40°C. The low temperature phase, which has been supposed to be trigonal, has a monoclinic symmetry. The lattice constants of each phase are shown in Table I.

(2) Two phase transitions near 17°C and -40°C can be clearly observed in the single domain crystal showing a thermal hysteresis in some extent, but the phase transitions of multidomain crystal show a complicated appearance, because the 17°C transition may be strongly affected by several factors, strain energy, domain wall energy etc., owing to the small difference between free energies in the room temperature phase and the triclinic phase.

(3) A small specific heat anomaly at 17°C transition and a considerable anomaly at -40°C transition are expected from the differential thermal curve.

(4) Electrical resistivity decreases with decreasing temperature in the room temperature phase and increases slightly at 17°C transition. It becomes more than ten times larger at -40°C transition and then shows a steep increase with decreasing temperature. The sudden increase of resistance at -40°C may be related to the considerable change of crystal structure expected from X-ray study.

The author wishes to express his hearty thanks to Prof. K. Tanaka of Kyoto University for his kind guidance and fruitful discussions. This work was supported in part by the Grant in Aid for the Fundamental Scientific Research from the Ministry of Education.

References

- 1) S. Nagasawa: *Denki Kagaku* **16** (1948) 13, 57.
- 2) B. T. Matthias and E. A. Wood: *Phys. Rev.* **84** (1951) 1255.
- 3) S. Sawada: *J. Phys. Soc. Japan* **11** (1956) 1237.
- 4) S. Sawada: *J. Phys. Soc. Japan* **11** (1956) 1246.
- 5) K. Hirakawa: *J. Phys. Soc. Japan* **7** (1952) 331.
- 6) M. Foëx: *Compt. rend.* **228** (1949) 1335.
- 7) S. Sawada and G. C. Danielson: *Phys. Rev.* **113** (1959) 803.
- 8) S. Tanisaki: *J. Phys. Soc. Japan* **11** (1956) 620.
- 9) S. Tanisaki: *J. Phys. Soc. Japan* **13** (1958) 363.
- 10) T. Iwai: private communication.
- 11) S. Tanisaki: *J. Phys. Soc. Japan* **15** (1960) 573.
- 12) K. Hirakawa and I. Ueda: *Mem. Fac. Sci. Kyusyu Univ. B*, **1** (1954) 112.
- 13) M. Ono: unpublished.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

Crystal Structure of Monoclinic Tungsten Trioxide at Room Temperature

By Sigetosi TANISAKI

Faculty of Literature and Science, Yamaguchi University

(Received November 27, 1959)

The crystal structure of tungsten trioxide at room temperature has been studied by the X-ray oscillation method. The crystal has a monoclinic unit cell with $a=7.30 \text{ \AA}$, $b=7.53 \text{ \AA}$, $c=7.68 \text{ \AA}$ and $\beta=90^\circ 54'$, containing eight molecules of WO_3 . c axis length is as twice as the values reported by the other authors. The space group is $P2_1/n$. The structure analysis was performed by trial and error based on inspection of the Patterson projections along a and c axes. The arrangement of tungsten atoms is similar to the structure reported by Braekken. The positions of oxygen atoms, which had been determined hitherto mainly from packing considerations, could be obtained directly from the weak reflections with odd index l . According to the obtained structure the crystal is antipolar in the directions of a , b and c axes.

§ 1. Introduction

Ever since tungsten trioxide, WO_3 , was first reported to be a ferroelectric by Nagasawa¹⁾ and Matthias²⁾, many investigations³⁾⁻⁶⁾ have been carried out about the properties of this material. The crystal structure of WO_3 in the room temperature phase was studied at first by Braekken⁷⁾, who described the structure as being triclinic (pseudomonoclinic) having two angles very nearly equal to 90° and the third showing a slight deviation from

this value and having the space group C_i . He determined the positions of the four tungsten atoms in the unit cell. But this structure corresponds to the monoclinic symmetry of space group $P2_1/a$ as pointed out by Anderson⁸⁾, who confirmed again the Braekken's structure. On the other hand, the structure analysis was also carried out by Ueda and Kobayashi⁹⁾ from a study of the Patterson projections. In spite of the coexistence of the space group $P2_1/a$, the atomic

arrangement of the Ueda and Kobayashi's structure is different from that of the Braekken's structure. According to Ueda and Kobayashi, the displacements along c direction of W atoms arranged parallel to b axis are in alternate sense, but W atoms arranged parallel to a axis displace in the same sense along c direction. On the contrary, in Braekken's structure the displacements along c direction of W atoms are in alternate sense in both a and b directions. Kehl et al.¹⁰⁾ studied the crystal structure of this material in tetragonal phase above 740°C by X-ray powder method and obtained the structure with the same feature as Braekken's type.

In order to investigate the mechanism of dielectric anomaly of this material it is very important to determine the correct crystal structure. In this work, a detailed X-ray analysis of room temperature monoclinic phase of WO_3 was carried out.

§ 2. Experimental Procedure

Oscillation photographs by 30°, in which a , b and c axes are vertical, were taken with Ni filtered $\text{CuK}\alpha$ radiation. Single crystals of WO_3 were grown by the method previously reported¹¹⁾. Relatively large single-domain crystals can easily be obtained from them by the appropriate external stress¹²⁾. Needle-shaped single-domain crystals with rectangular cross section in which a was parallel to the needle axis were prepared by cleavage in (010) from a large single-domain crystal. One of them was used for a vertical oscillation photographs. Then by cutting another needle crystal in (100), a single-domain crystal suitable for c vertical oscillation was obtained. The crystal for b vertical oscillation was obtained by the following method. Several crystals in which a axis was parallel to needle axis were heated up to the tetragonal phase over 740°C, and then cooled down to room temperature. Then by chance the needle axis changed from a to b , but in this case it was not easy to obtain the single domain crystal by the external stress owing to its very minute dimension, so that the multidomain crystal was used for b vertical oscillation. Crystals used in this experiment have approximately uniform rectangular cross sections, which can be determined accurately by microscopic measurements. The cross sec-

tions of each crystal are as follows:

$73 \times 38 \mu^2$ (length about 2 mm)	for a vertical,
$70 \times 73 \mu^2$ (length about 1.5 mm)	for b vertical,
$171 \times 236 \mu^2$ (length about 0.2 mm)	for c vertical.

Intensities were visually estimated using the multifilm technique with an intensity scale only for the equator reflections of each film, because it is only in these cases that a reliable absorption correction could easily be applied according to the graphical method reported by Howells¹³⁾. The linear absorption coefficient of WO_3 for $\text{CuK}\alpha$ radiation was calculated to be $\mu = 1005 \text{ cm}^{-1}$ from atomic absorption coefficients. As for the crystal used for b vertical, in order to take account of the effect of domain structure, the following device was used for the determination of reflection intensity from oscillation photographs.

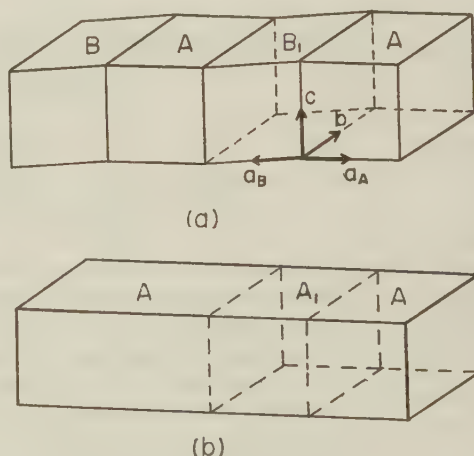


Fig. 1. (a) Schematic representation of multidomain crystal with walls of (100) twin planes. (b) Single-domain crystal corresponding to (a).

The crystal was composed of two kinds of domains, A and B, twinned by (100) as shown in Fig. 1(a) schematically. Let us imagine the corresponding single-domain crystal of A domain only as shown in Fig. 1(b), in which the part A_1 corresponds to the domain B_1 of the multidomain crystal, and compare the reflections from each crystal. The external forms of both crystals are almost the same, for the crystal is monoclinic and β is nearly equal to 90°. Therefore, when we consider the directions of incident and reflected beams

it is evident that the effect of absorption for $(h0l)_A$ reflection from the part A_1 of single-domain crystal is not equal to that for $(h0l)_B$ reflection but nearly equal to that for $(\bar{h}0\bar{l})_B$ reflection from the domain B_1 of multidomain crystal. Accordingly in order to obtain the intensity of $(h0l)$ reflection, we must sum up the intensities of $(h0l)_A$ from A domains and that of $(\bar{h}0\bar{l})_B$ from B domains and then apply the usual absorption correction to the summation.

The structure analysis was performed by trial and error method based on inspection of the Patterson projections along a and c axes. The corrections of temperature factors and the effects of extinction were ignored. For the scattering factors of the atoms involved,

the values tabulated in the Internationale Tabellen (1935) were used.

§ 3. Structure Analysis

1) Symmetry and unit cell dimensions

The observed data require the monoclinic structure whose unit cell dimensions calculated from the back reflections of (092), (920), (804) and $(80\bar{4})$ are

$$a=7.30 \text{ \AA}, \quad b=7.53 \text{ \AA}, \quad c=7.68 \text{ \AA} \\ \text{and } \beta=90^\circ 54',$$

and unit cell contains eight molecules of WO_3 . These values are in good agreement with the results of the other investigators^{7)–9), 14)}, except that the c axis length is as twice as the other's values. Single crystal rotation photographs for c axis show quite clearly weak first and third order layer lines for c axis of 7.68 Å. The reason for the discrepancy of c axis length is not clear, but the crystal obtained by Sawada and Danielson⁶⁾, which was kindly offered by Sawada, has the same twice length of c axis.

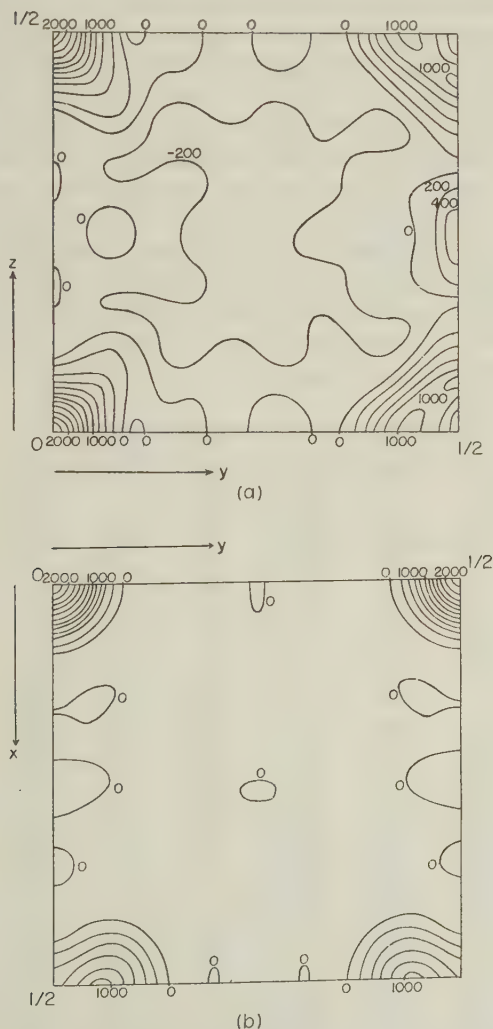


Fig. 2. Patterson projections along (a) a axis and (b) c axis. Contour lines are in arbitrary scale.

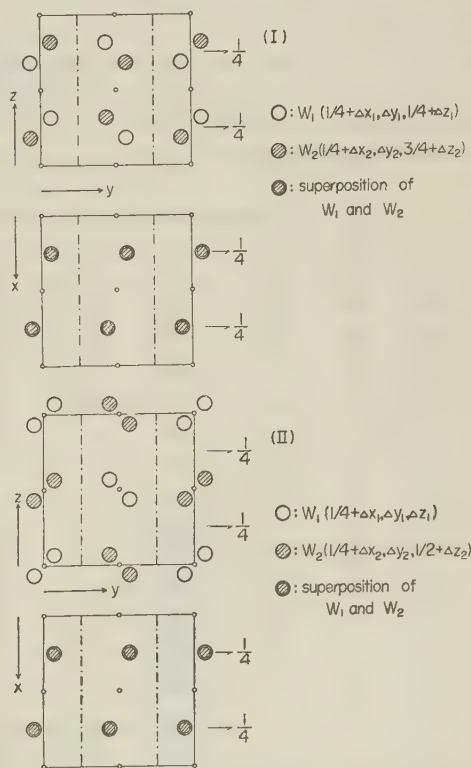


Fig. 3. Two types of possible arrangements of W atoms from inspection of Patterson projections.

Reflections ($h0l$) were all absent when $h+l=2n+1$, and reflections ($0k0$) were all absent when $k=2n+1$. These absences are characteristic of the space group $P2_1/n-C_{2h}^5$.

2) Atomic positions

Patterson maps for the projections along a and c axes shown in Fig. 2 were calculated from ($0kl$) and ($h00$) reflections in order to get the informations as to the positions of heavy tungsten atoms. It is impossible to get informations relating to W-O distances and O-O distances from Patterson maps, for the oxygen atoms are too light compared with tungsten atoms. Taking consideration of the space group $P2_1/n$, there are two models of the possible arrangements of W atoms from the inspection of Patterson maps, which are shown in Fig. 3. The approximate parameters of W atoms are as follows:

model (I) $W_1=1/4+\Delta x_1, \Delta y_1, 1/4+\Delta z_1$

$W_2=1/4+\Delta x_2, \Delta y_2, 3/4+\Delta z_2$

model (II) $W_1=1/4+\Delta x_1, \Delta y_1, \Delta z_1$

$W_2=1/4+\Delta x_2, \Delta y_2, 1/2+\Delta z_2$

and in each model $\Delta x_1 \doteq 0, \Delta x_2 \doteq 0, \Delta y_1 \doteq \Delta y_2 \doteq 0.03$ and $\Delta z_1 \doteq \Delta z_2 \doteq 0.03$. If the relations $\Delta x_1=\Delta x_2=0, \Delta y_1=\Delta y_2$ and $\Delta z_1=\Delta z_2$ are strictly satisfied, both models correspond to the identical structure of Braekken's type in so far as the arrangement of W atoms except the

translation of the origin of $1/4$ along z direction. Since the observed reflections with odd index l are very faint, they may be ignored in the first stage and it is assumed to be $\Delta x_1=\Delta x_2=0, \Delta y_1=\Delta y_2=\Delta y, \Delta z_1=\Delta z_2=\Delta z$. Then parameters of W atoms were calculated by trial and error using the disagreement factor $R=(\Sigma||F_0|-|F_c||)/\Sigma|F_0|$ as a criterion. The scale K for F_0 is established by $K=\Sigma|F_c|/\Sigma|F_0|$. In this calculation the positions of O atoms were assumed to be half way between neighbouring W atoms in accordance with Braekken's assumption. Obtained values of Δy and Δz are as follows:

$$\Delta y=0.030, \quad \Delta z=0.033.$$

The weak reflections with odd index l must be taken into consideration in the next stage. Then there are two cases; case (1) in which the arrangement of W atoms is just equal to that above described and the reflections with odd index l are due to O atoms only, and case (2) in which W atoms show the small displacements from the arrangement above described. The intensity contribution of O atoms to the reflections which have relatively large values of $\sin \theta/\lambda$ is to be small. But among such reflections with odd index l there are rather strong ones, for example (507) and (075). Therefore the case (1) should be excluded.

Table I. Comparison between calculated and observed structure factors of ($0kl$).

$0kl$	$ F_c $	$ F_0 $	$0kl$	$ F_c $	$ F_0 $	$0kl$	$ F_c $	$ F_0 $	$0kl$	$ F_c $	$ F_0 $
002	542	502	023	25	25	042	301	296	063	32	23
004	381	407	024	283	268	043	35	30	064	110	100
006	138	141	025	10	15	044	228	195	065	15	—
008	14	—	026	92	91	045	16	23	066	40	48
			027	17	15	046	93	91			
011	7	—	028	34	22	047	26	26	071	23	22
012	33	45							072	119	128
013	12	—	031	16	17	051	16	18	073	27	17
014	58	76	032	87	102	052	115	136	074	211	219
015	11	—	033	23	20	053	14	—	075	52	50
016	59	87	034	153	141	054	203	184	076	245	242
017	2	—	035	31	32	055	27	31			
018	57	78	036	161	171	056	224	238	080	31	41
019	11	—	037	20	17	057	18	17	081	4	—
			038	150	171				082	19	30
020	550	511				060	184	184			
021	18	20	040	393	405	061	19	19	091	20	20
022	381	348	041	25	29	062	144	121			

observed intensities even if the contribution of O atoms was taken into account, and so the model (I) was adopted.

The contribution of W atoms for the reflections with odd index *l* is so small that the oxygen contribution is generally a comparable order with them. Therefore, in order to calculate the structure factors, the arrangement of O atoms must be taken into account. In other words, the positions of O atoms, which had been determined mainly from packing considerations, could be obtained directly from X-ray reflections. Atomic coordinates in fractions of the cell edges obtained by trial and error are as follows:

W ₁	1/4+0.002	0.026	1/4+0.035
----------------	-----------	-------	-----------

W ₂	1/4-0.003	0.033	3/4+0.031
O _{x1}	0	0.025	1/4-0.030
O _{x2}	0	1/2-0.025	1/4-0.030
O _{y1}	1/4+0.040	1/4+0.040	1/4+0.015
O _{y2}	1/4-0.040	1/4+0.040	3/4-0.015
O _{z1}	1/4+0.030	0.040	0.030
O _{z2}	1/4+0.030	1/2-0.010	-0.030

Among these values, *y* coordinates of O_{x1} (*Δy*₁) and O_{x2} (1/2-*Δy*₂) and *x* coordinates of O_{y1} (1/4+*Δx*₁) and O_{y2} (1/4-*Δx*₂) could not be determined only from the intensities of equator reflections with odd index *l*. From the equator reflections it was only concluded that *Δy*₁=*Δy*₂ and *Δx*₁=*Δx*₂. Since the quantitative

Table IV. Comparison between calculated structure factors and observations of (*hkl*).

<i>hkl</i>	<i>F</i> _o	obs.	<i>hkl</i>	<i>F</i> _o	obs.	<i>hkl</i>	<i>F</i> _o	obs.	<i>hkl</i>	<i>F</i> _o	obs.
111	2	-	241	26	-	471	35	+	611	26	+
121	4	-	251	18	-				621	14	-
131	43	+	261	19	-	411	18	-	631	31	+
141	22	+	271	10	-	421	17	-	641	20	-
151	26	+	281	4	-	431	28	-	651	7	-
161	39	+				441	24	-	661	15	-
171	20	+	311	33	+	451	14	-			
181	53	+	321	25	+	461	18	-	711	25	+
			331	5	-	471	11	-	721	8	-
111	12	-	341	33	-				731	12	-
121	8	-	351	22	+	511	24	+	741	26	+
131	1	-	361	43	+	521	13	-	751	38	+
141	24	+	371	23	-	531	16	-			
151	6	-	381	53	+	541	25	-	711	28	+
161	41	+				551	6	-	721	6	-
171	1	-	311	40	+	561	38	+	731	18	-
181	51	+	321	14	-				741	16	-
			331	24	+	511	28	+	751	44	+
211	19	-	341	10	-	521	2	-			
221	14	-	351	46	+	531	1	-	811	40	+
231	40	+	361	32	+	541	15	-	821	12	-
241	23	-	371	40	+	551	21	-	831	47	+
251	12	-	381	48	+	561	32	+			
261	18	-							811	30	+
271	31	+	411	31	+	611	36	+	821	13	-
281	10	-	421	14	-	621	13	-	831	37	+
			431	48	+	631	48	+			
211	7	-	441	21	-	641	20	-			
221	19	-	451	11	-	651	13	-			
231	11	-	461	18	-	661	18	-			

+ = observed reflection, - = absent reflection.

c axis in alternate sense but W atoms arranged parallel to c axis show only a very little displacement in each other. The locations of W-W peaks in the Patterson map projected along a axis expected from the Ueda and Kobayashi's structure are entirely different from those in Fig. 2(a), though the expected peaks in the projection along c axis are in accordance with those in Fig. 2(b). The intensity relation $I(h0l) > I(h0\bar{l})$ for even index l which was pointed out by them as one of the grounds of their structure is also satisfied by our structure. Therefore it seems that the Ueda and Kobayashi's structure is unlikely, and then the inconsistency with the structure of high temperature phase reported by Kehl *et al.* can be excluded.

There have been many reports in relation to the ferroelectricity or antiferroelectricity of this material. But owing to the high electric conductivity, the accurate dielectric measurement is very difficult and it has not been determined whether WO_3 is ferroelectric or antiferroelectric at room temperature. Of course it is impossible to determine the ferroelectricity or antiferroelectricity from the crystal structure alone, from which we can only determine whether the crystal is polar or nonpolar. According to the structure above determined, WO_3 is a nonpolar crystal with centers of symmetry, and so it can not be ferroelectric or ferrielectric at room temperature.

In relation to the antiferroelectricity, it is interesting to examine the W-O distances. The crystal is composed of two kinds of WO_6 octahedra, one of which has a W_1 atom in its center and another has a W_2 atom. The unit cell contains eight octahedra, four of one kind and four of another kind. These octahedra are arranged in the crystal in such a way that a shorter distance and a longer one are linked alternately in any of three directions parallel to a , b and c axes as shown in Fig. 5 and in this sense we may say that the crystal is antipolar along the a , b and c directions. The differences between the longer distances and the shorter ones along a and b axes are considerably larger than that along c axis. Therefore, if the crystal is antiferroelectric at room temperature, it is probable that the polar axis is parallel to a or b axes or otherwise it is in the plane (001), though

hitherto it has been thought that the polar axis may be parallel to c axis.

In conclusion the author wishes to express his hearty thanks to Prof. K. Tanaka of Kyoto University for his kind guidance and fruitful discussions, and to Mr. H. Onomichi for his assistance. This work was supported in part by the Grant in Aid for the Fundamental Scientific Research from the Ministry of Education.

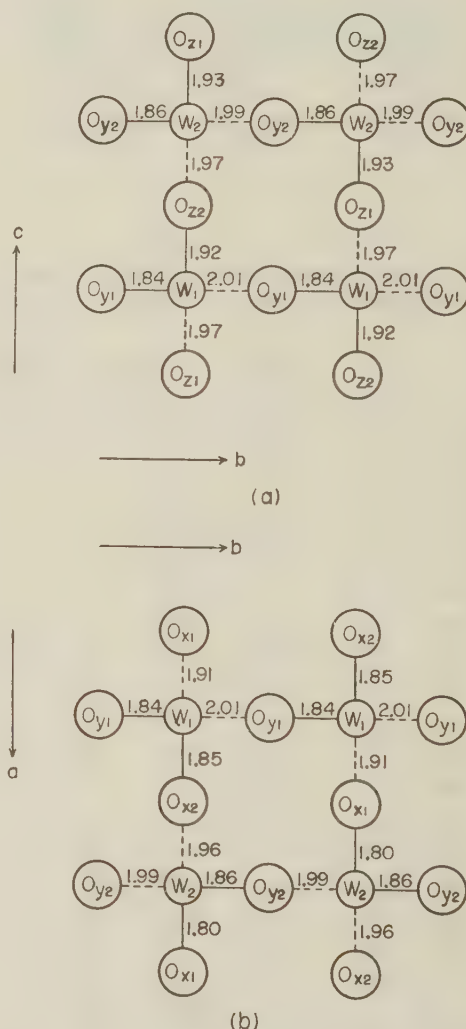


Fig. 5. W-O distances given in Å in the layers of (a) $x \approx 1/4$ and (b) $z \approx 1/4$. Full lines and broken lines show the shorter distances and the longer ones respectively.

References

1. S. Nagasawa: *Denki Kagaku* **16** (1948) 13, 57.
2. B. T. Matthias: *Phys. Rev.* **76** (1949) 430.

- 3) B. T. Matthias and E. A. Wood: Phys. Rev. **84** (1951) 1255.
- 4) K. Hirakawa and I. Ueda: Mem. Fac. Sci. Kyusyu Univ. **B**, **1** (1954) 112.
- 5) S. Sawada: J. Phys. Soc. Japan **11** (1956) 1237, 1246.
- 6) S. Sawada and G. C. Danielson: Phys. Rev. **113** (1959) 803, 1005, 1008.
- 7) H. Braekken: Z. Krist. **78** (1931) 484.
- 8) G. Anderson: Acta Chem. Scand. **7** (1953) 154.
- 9) R. Ueda and J. Kobayashi: Phys. Rev. **91** (1953) 1565.
- J. Kobayashi: Mem. Sch. Sci. and Eng. Waseda Univ. **18** (1954) 92.
- 10) W. L. Kehl, R. G. Hay and D. Wahl: J. Appl. Phys. **23** (1952) 214.
- 11) S. Tanisaki: J. Phys. Soc. Japan **11** (1956) 620.
- 12) S. Tanisaki: J. Phys. Soc. Japan **13** (1958) 363.
- 13) R. G. Howells: Acta Cryst. **3** (1950) 366.
- 14) J. A. Perri, E. Banks and B. Post: J. Appl. Phys. **28** (1957) 1272.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

Magnetic Properties of Iron Phosphide Fe_2P

By Shū CHIBA^{*)}

*The Research Institute for Iron, Steel and Other Metals,
Tohoku University, Sendai*

(Received March 19, 1959)

The magnetic properties of iron phosphide, Fe_2P , were investigated. It was found by means of a newly designed apparatus for the measurement of magnetization that the extrapolated saturation magnetization at absolute zero of temperature reaches 66.3 gauss per gram of iron, corresponding to a spin moment of 0.85 ± 0.02 Bohr magneton per iron atom. The ferromagnetic Curie point is at 306°K. The Curie-Weiss law holds up to 900°K with the paramagnetic Curie point 478°K and the effective magneton number is 3.2 ± 0.2 . A brief remark is given for these data.

§ 1. Introduction

The phase diagram of the iron-phosphorus system was hitherto investigated by several authors.^{**)} Three compounds, Fe_3P (15.62% P), Fe_2P (21.74% P) and FeP (35.71% P) were found in this system. Fe_3P and Fe_2P were known to be ferromagnetic with their Curie points at 693°K and 353°K respectively, while the compound FeP showed paramagnetic behavior. The crystal structure of the compound Fe_2P was investigated by Hägg¹⁾ as well as by Hendricks and Kosting.²⁾ According to their results, Fe_2P has a rather peculiar structure as compared with the

usual ionic crystals. Interatomic distances between the anions and cations in the crystal lattice are too short to be understood from the usual conception of ionic radii. As to the magnetic properties, only the Curie point, 353°K, has hitherto been reported.³⁾ The present paper reports the results of the measurements of the saturation magnetization, susceptibility and electric resistance for the compound Fe_2P , brief data are also given for FeP . For the measurement of the saturation magnetization, susceptibility and electric resistance for the compound Fe_2P , brief data are also given for FeP . For the measurement of the saturation magnetization, a newly designed handy apparatus was used.

§ 2. Preparation of Specimens

Specimens in the present experiment were prepared by the ceramic method described

^{*)} Now at the Matsuda Research Laboratory of Tokyo-Shibaura Electric Co., Ltd.

^{**)} A summary of the metallographical researches hitherto reported is given by M. Hansen: (Construction of Binary Alloys, 2nd Edition (1958), 692).

below. Powders of electrolytic iron (150 mesh) with purity of 99.9% were weighed in desired proportions, mixed well in a mortar and enclosed in evacuated silica tubes. Impurities in red phosphorus were mainly water and phosphoric acid, which would not introduce any appreciable errors to the result of the following magnetic measurement. Since the boiling point of red phosphorus is 416°C , rapid heating of these mixtures above this temperature may induce an abrupt explosion of the reaction tube, due to the reaction heat and the vapour pressure of phosphorus. Therefore these mixtures were fired in the electric furnace initially at 400°C for 24 hours and then heated up to 1000°C at a slow rate of 20 degrees per hour. In this way several specimens from Fe_2P to FeP were prepared. The compositions of the specimens were determined by chemical analysis. They are shown in Table I.

Table I.

Specimen No.	1	2	3	4	5
Result of Analysis (Atomic percent of phosphorus)	50.1	44.5	40.1	36.4	33.4

Debye powder photograph was taken for the specimen No. 5, i.e., Fe_2P specimen. The diffraction line were completely indexed as a hexagonal lattice with $a=5.852\text{\AA}$, $c=3.453\text{\AA}$, and $c/a=0.590$. The observed line intensities also coincided with those derived from the proposed structure by Hägg⁽¹⁾ as well as Hendricks and Kosting.⁽²⁾

§ 3. Experimental Apparatus

For the purpose of measuring saturation magnetization of the specimens at various temperatures by means of an electromagnet, a handy apparatus was designed by the author. The apparatus is of an induction type, the details of which are described below.

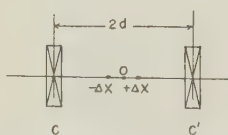


Fig. 1. Measuring Principle.

A pair of search coils C and C' are wound on the front surfaces of the pole pieces of the electromagnet, as shown in Fig. 1. Both coils are designed to be exactly equal and connected in antiphase series so as to compensate the induced e.m.f. due to the field fluctuation of the electromagnet. The specimen is set on the common axis of the coils, and then displaces along the axis. If the specimen is regarded as a magnetic dipole and if it moves from $-\Delta x$ to $+\Delta x$ along the axis of the pair of search coils (as shown in Fig. 1), the change of flux ΔF passing through the coils due to such displacement is given by

$$\Delta F = k \Delta x$$

and

$$k = 24\pi m N_p^2 \left\{ \frac{1}{(a^2 + d^2)^{5/2}} \right\},$$

where a and N are the radius and the number of windings of each coil respectively, m is the magnetic moment of the dipole and $2d$ is the distance between the two coils. It can also be proved that the correction arising from the size of specimen is negligibly small as compared with the dipole term shown above. Hence, if the induced e.m.f. due to the motion of the specimen is measured, then the magnetization of the specimen can be calculated.

The detailed parts of the apparatus are shown in Fig. 2. A lever, 900 mm in length hangs on the fulcrum O . The lever is composed of two parts, the upper side being made of brass and the lower side of a quartz rod. A disc-formed specimen S (10 mm in diameter and 1.5 mm in thickness) is attached to the bottom of the lower side of the lever and moved by a cam K attached to the head of the lever. A stopper T of the lever is adjustable in accordance with the required sensitivity. A phase switch P is of use in securing constant conditions for repetitive movements of the lever. Search coils C and C' on the pole pieces of the electromagnet are 26 mm in mean diameter and have 600 windings of enamelled copper wire with 0.1 mm in diameter.

Measurements of the magnetic moment at liquid nitrogen temperature are made by covering the specimen container D with a copper cylinder A , which is cooled by liquid nitrogen in a vessel V attached to A . In

this way the temperature of the specimen can be kept slightly higher than the boiling temperature of liquid nitrogen; intermediate temperatures are also reached by adjusting the height of vessel *V*. The measurements at high temperatures can be made by use of a non-inductive electric furnace.

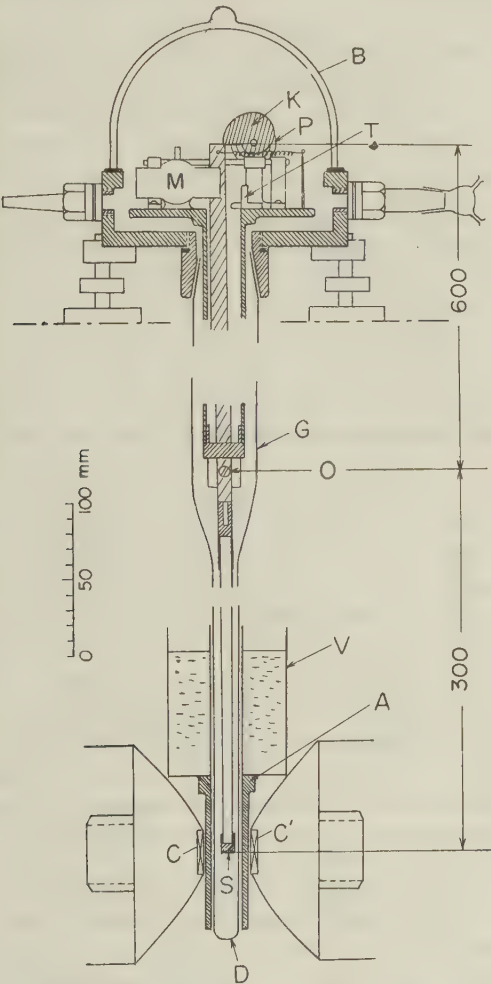


Fig. 2. The newly constructed apparatus for measuring saturation magnetization.

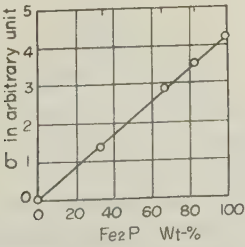


Fig. 3. Saturation values in arbitrary units of various specimens against Fe_2P -concentration.

Paramagnetic susceptibility above the Curie point was measured up to 942°C by a magnetic balance⁴⁾ of automatically recording type.

§ 4. Experimental Results

Magnetizations of various specimens, No. 1 to No. 5, at the field strength of 10,000 *Oe* and at room temperature are shown in Fig. 3. The abscissa of the figure is the concentration of Fe_2P . In the figure the magnetization changes linearly with the concentration of Fe_2P .

Now the magnetization of the compound Fe_2P was measured in various fields with varying temperature. For the determination of the moment at absolute zero of temperature it was assumed that the magnetization could be expressed approximately in terms of temperature *T* and applied magnetic field *H* as follows:

$$\sigma = \sigma_{\infty}(1 - aT^2)\left(1 - \frac{b}{H^2}\right)$$

First, in order to show the temperature dependence of the magnetization, σ is plotted against T^2 for a constant field in Fig. 4. It was found that the measured magnetization changes almost linearly with the square of temperature, and the magnetizations at absolute zero temperature in various magnetic fields can be obtained by extrapolation. In Fig. 5, the magnetizations at 0°K thus obtained are plotted against the inverse square of

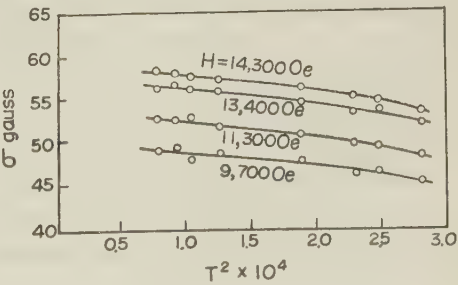


Fig. 4. The T^2 law Fe_2P .

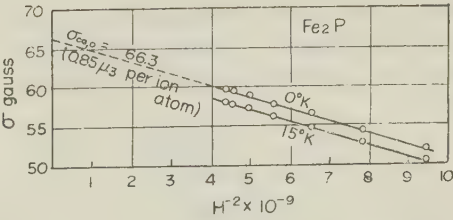


Fig. 5. The curve of σ versus H^{-2} of Fe_2P .

field, which shows that they change also linearly with the inverse square of the magnetic field. The saturation value at absolute zero of temperature is determined to be (66.3 ± 1.5) gauss per gram of iron atom, corresponding to (0.85 ± 0.02) Bohr magneton and to a spin of $(0.85 \pm 0.02)/2$ per iron atom.

The temperature dependence of magnetization of Fe_2P is studied under an applied field of 10,000 Oe in the region from 87 to 335°K. The result is shown in Fig. 6. From this curve it can be said that the ferromagnetic Curie point is 306°K, in discordance with the value reported by Le Chaterier and Wologdine³⁾ 353°K.

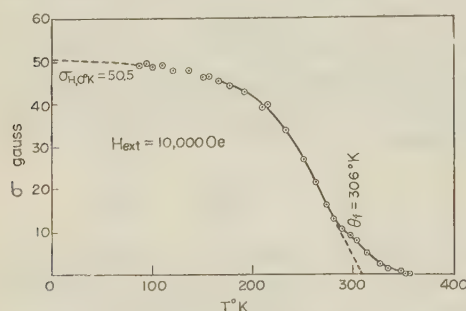


Fig. 6. The curve of magnetization *vs.* temperature under 10,000 Oe.

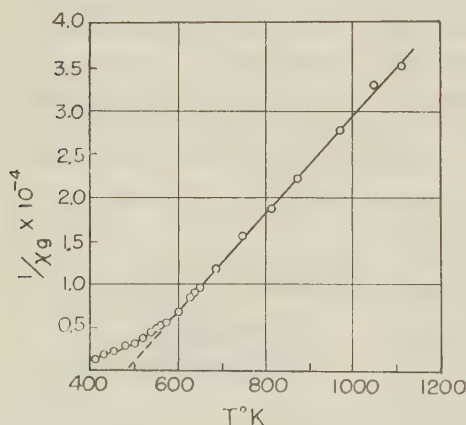


Fig. 7. Inverse susceptibility for iron phosphide Fe_2P .

The result of the measurement of susceptibility χ_g for Fe_2P above the Curie point is shown in Fig. 7. Above ca 570°K, the susceptibility changes according to the Curie-Weiss law;

$$\chi_{mol}^* = \frac{1.28 \pm 0.06}{T - (478 \pm 10)}$$

* χ_{mol} refers to one gram ion of Fe , viz., one mole of $FeP_{0.5}$.

Between the ferromagnetic Curie point and ca 570°K, the $1/\chi - T$ curve bends upwards as like an ordinary ferromagnetic substance. From the Curie constant, the number of the effective Bohr magneton is found to be 3.2 ± 0.2 . This corresponds to a spin value of $(2.4 \pm 0.2)/2$, provided that the orbital moment is quenched.

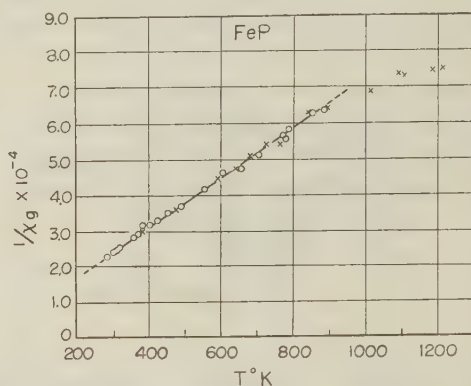


Fig. 8. Inverse susceptibility of FeP per gram.

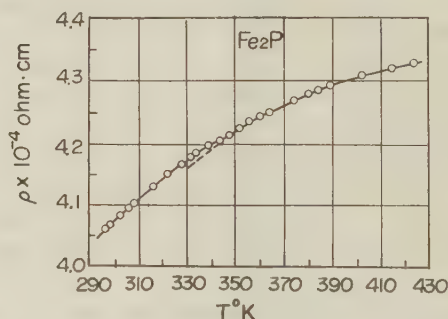


Fig. 9. Electric resistance *vs.* temperature curve of Fe_2P .

The susceptibility of FeP was measured in the temperature range from room temperature to 1200°K, and the results are shown in Fig. 8. As is shown, the inverse susceptibility changes linearly with the temperature so that the susceptibility obeys the following formula up to 900°K.

$$\chi_{mol} = \frac{1.46}{T + 50}$$

Above 900°K, the Curie-Weiss law does not hold. This is probably due to some phase transition present in this range of temperatures. In the measurements during cooling at the rate of two degrees per minute, we could find no thermal hysteresis below 900°K.

Electric resistance was measured from room temperature to 424°K; it increases with tem-

perature, as shown in Fig. 9. The specific resistivity at room temperature is about 4×10^{-4} ohm cm.

§ 5. Discussion

As was mentioned in the introduction, interatomic distances in this crystal are fairly smaller than would be expected from the ionic picture: There are two crystallographically different Fe atom positions, Fe_A and Fe_B . Fe_A site is located at the centre of a distorted tetrahedron, four P atoms occupying its vertices, two of which are $2.22\text{\AA}$, and the other two $2.30\text{\AA}$ apart from the central atom. Another site, Fe_B , is surrounded by three P atoms, two of which are $2.21\text{\AA}$, the remaining one is $2.34\text{\AA}$ apart from the metal atom. Then, if we were to consider the crystal to be ionic, e.g. as $Fe^{3+}FeP^{3-}$, and use Pauling's radii,* the shortest $Fe-P$ distance would be equal to $2.72\text{\AA}$, which is far larger than any of the interatomic distances in the actual crystal mentioned above. That this compound cannot be regarded as an ionic crystal is also borne out by our magnetic data. Both the Curie constant and the saturation magnetization are definitely smaller than those expected from the ionic picture. The average spin value for iron atoms calculated from the former constant is $(2.4 \pm 0.2)/2$ and that based on the latter $(0.85 \pm 0.02)/2$, respectively, while they should be $3.75/2^{**}$ and $3.5/2$, provided that the moments of Fe^{3+} and Fe atoms couple ferromagnetically. Of course the satu-

ration value could be made smaller by assuming a ferromagnetic coupling between Fe^{3+} and Fe spins, but the Curie-Weiss behavior of the inverse susceptibility data may probably rule out this possibility. Hence, the magnetic properties may rather be depicted better by the collective electron model than the ionic lattice picture. The collective electron picture may be supported by the low electrical resistivity, 4×10^{-4} ohm cm at room temperature. In such a model, the origin of small saturation magnetization at low temperatures might be understood if a relatively small exchange energy could be assumed between neighboring metal atoms. It may be noted that the shortest $Fe-Fe$ distance in the crystal, $2.65\text{\AA}$, is only a little longer than those observed in metals ($\sim 2.5\text{\AA}$).

Acknowledgements

The author wishes to express his hearty thanks to Profs. T. Hirone, H. Watanabe, and S. Nagasaki for their kind guidance and discussion and to Prof. S. Maeda for his guidance and advice on the construction of the newly designed apparatus.

References

- 1) G. Hägg, Z. Krist. **68** (1928) 470.
- 2) S. B. Hendricks and P. Q. Kisting: Z. Krist. **74** (1930) 522.
- 3) H. Le Chaterir and S. Wologdine: Compt. rend. **149** (1909) 709.
- 4) T. Hirone, S. Maeda and N. Tsuya: Sci. Rep. RITU A, **6** (1954) 67.

* Fe^{3+} ; $0.60\text{\AA}$, P^{3-} ; $2.12\text{\AA}$.

** $\bar{S}(\bar{S}+1) = 1/2(S(S+1) + S'(S'+1))$ with $S=5/2$, $S'=1$.

Internal Friction of Quartz.

By Yosio HIKI

*The Government Mechanical Laboratory, Suginami-ku,
Tokyo, Japan*

(Received November 14, 1959)

The internal friction of transparent natural quartz was measured at room temperature with longitudinal vibration in kilocycle range using a composite piezo-electric oscillator. Specimens were cylinders axes of which took various orientations in the crystallographic YZ-plane. The internal friction of specimens parallel to the Y- or Z-axis was small and almost independent of the strain amplitude of the vibration, while that of specimens with other orientations was rather large and showed marked dependence on the amplitude. The experimental results were analyzed with the theory of dislocation damping based on the pinned-down dislocation model. It could be concluded that the internal friction of quartz was mainly due to the vibration of dislocations in the slip plane parallel to the Y- or Z-axis. The dislocation density in a specimen was estimated to be 10^3 – 10^4 cm⁻². It was also found that the dislocation density was reduced by annealing the specimen. The defects pinning down the dislocations were assumed to be aggregates of metallic impurities.

§ 1. Introduction

There have been some investigations on the internal friction of quartz crystals. Artman¹⁾, Alers²⁾, Cook *et al.*³⁾ and Wasilik⁴⁾ measured the decrement of quartz bars in longitudinal or torsional vibrations, and observed one relaxation peak at high temperatures (near 300°C at 36 kc/sec). Some of the authors³⁾ interpreted these phenomena as due to the stress induced migration of the metallic impurity ions in the lattice. Bömmel *et al.*⁵⁾, King⁶⁾ and White⁷⁾ measured Q^{-1} of quartz plate vibrating in shear, and revealed the presence of two relaxation peaks at low temperatures (near 21 and 52°K at 5 Mc/sec). Mason⁸⁾ discussed that the lower temperature peak could be identified with so-called Bordoni's peak arising from the movement of dislocations, while the higher temperature peak was originated from the vibration of oxygen atoms in the quartz lattice. Fitzgerald⁹⁾ determined the complex shear compliance of quartz crystals as a function of frequency, and discovered sharp resonance dispersions in the audio-frequency range (100–5000 c/sec). Some of these resonances may be related with the presence of crystal imperfections.

In the present investigation, the internal friction of single crystals of quartz with

various crystallographic orientations was measured as a function of the strain amplitude of the vibration at room temperature, since the systematic measurements of the amplitude-dependence have not yet been carried out.

§ 2. Experimental Procedures

It is very difficult to determine the internal friction of quartz, since the value is so small that other sources of dissipation of energy frequently predominate over the true internal loss of the specimen. The resonance method is most adequate because of possibility to minimize the external losses. The Marx's three-component piezo-electric oscillator method⁹⁾ was used in the present experiment. The frequency of vibration used was about 64 kc/sec. The details of the experiments were similar to those described in the earlier paper¹⁰⁾. The different situation was that the energy loss of the measuring quartz oscillator system, being of the order of 10^{-5} , could not be neglected in comparison with the internal friction of the quartz specimens. Soon after a run of measurement about a specimen was carried out, the specimen was detached from the oscillator and the internal friction of the oscillator system was measured. The internal friction of the specimen can be obtained

from the equation $\delta_s m_s = \delta_t m_t - \delta_o m_o$, where δ 's and m 's represent the internal friction and the mass of each element, and suffixes s , t and o refer to specimen, total and oscillator, respectively.

Specimens were prepared from transparent Brazilian quartz crystals exclusive of the part containing twins or other visible defects. The metallic impurities in three mother crystals were determined by the spectroscopic analysis and the results were as show in Table I. The specimens were cylindrical form of 2 mm in diameter and about 40–50 mm in length. The length was adjusted so as to make its frequency of vibration coincide

with that of quartz oscillator within 1%. The direction of the specimen axis was chosen to be in the crystallographic YZ-plane and made the angle θ with Y-axis, as shown in Fig. 1. X, Y and Z are the orthogonal axes and sometimes called as the electrical, mechanical and optical axes, respectively. Sixteen specimens with various orientations were prepared from various mother crystals, the angle θ being 0° , 18.5° , 45° , 60° , 71.5° or 90° . The specimens will hereafter be designated, for example, as "A-45-1", which refers to that "mother crystal is 'A', angle θ equals to 45° , and specimen number is 1".

§ 3. Results and Discussions

3.1 Results on amplitude-dependence

The internal friction of quartz, δ , was measured as a function of the strain amplitude of vibration, ϵ . Some of the typical results for various specimens are shown in Fig. 2. In the case of specimens parallel to the Y- or Z-axis, namely, when $\theta=0^\circ$ or 90° , the values of the internal friction are small and almost independent of the strain amplitude. The internal friction of specimens

Table I. Concentration of impurities in ppm.

	A	F	H
Al	10– 50	50–100	100–500
Ba	50–100	10– 50	tr.
Bi	5– 10	nil	1– 5
Ca	nil	50–100	tr.
Cu	1– 5	5– 10	1– 5
Fe	10– 50	5– 10	5– 10
Ga	1– 5	nil	1– 5
Ge	1– 5	nil	tr.
K	10– 50	10– 50	100–500
Li	nil	nil	tr.
Na	10– 50	50–100	10– 50
Pb	nil	10– 50	5– 10
Sn	5– 10	nil	tr.
Sr	nil	tr.	nil
Ti	tr.	nil	nil

Ag, As, Au, B, Be, Cd, Co, Cr, In, Mn, Mo, Ni, Sb, Tl, V, W, Zn, Zr were not detected.

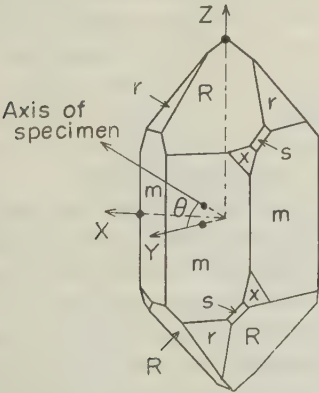


Fig. 1. Quartz crystal (right-quartz) with orthogonal axial system.

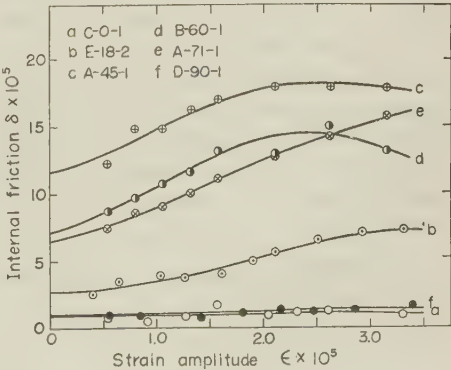


Fig. 2. Internal friction *vs* strain amplitude curves for various specimens.

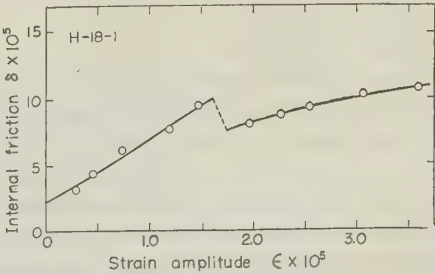


Fig. 3. Internal friction *vs* strain amplitude curve for specimen 'H'.

with other orientations is rather large and depends markedly on the strain amplitude. In general, δ increases monotonously with increasing ε . At large amplitude, however, it seems sometimes to decrease slightly. Specimens made from mother crystal 'H' show anomalous discontinuities in the δ vs ε curves, as shown in Fig. 3.

3.2. Dislocation damping in crystals

The amplitude-dependent internal friction was frequently observed in single crystals of pure metals. Such behavior was sometimes interpreted as due to the dislocation damping, namely, the dissipation of mechanical energy originated from the motion of dislocations. Granato and Lücke¹¹⁾ have developed a theory about the dislocation damping and made a comprehensive analysis of experimental results. They start from a model that crystalline solid contains a network of dislocations, their intersections being immovable. The dislocation lines are further pinned down or fixed by point defects which exert forces on them. They conclude that the internal friction is expressed as the sum of the frequency-dependent and amplitude-independent term, δ_i , and the frequency-independent and amplitude-dependent term, δ_h . The former corresponds to the dynamic loss due to the damping force against the movement of the dislocation, while the latter corresponds to the static hysteresis loss originated from the break-away of the dislocation line from the pinning point. These are given by^{11), 12)}

$$\delta_i = \frac{5! \Omega A_0}{\pi^2 c} A L_e^4 B \omega; \quad L_e = 3.31 L_c, \quad (1)$$

$$\left. \begin{aligned} \delta_h &= \frac{c_0}{\varepsilon^{1/2}} \exp(-c_1/\varepsilon); \\ c_0 &= \frac{2\Omega A_0}{\pi^2} \left(\frac{F}{bsE} \right)^{1/2} \frac{A L_n^3}{L_c^{3/2}}, \\ c_1 &= \frac{2F}{\pi bsE} \frac{1}{L_c}, \end{aligned} \right\} \quad (2)$$

where ω is the angular frequency of the vibration and ε the strain amplitude of the specimen. $A_0 = 4(1-\nu)/\pi^2$, $c = 2Gb^2/\pi(1-\nu)$ and E is Young's modulus along specimen axis, G shear modulus along slip direction, ν Poisson's ratio, b Burgers vector. Ω is orientation factor, s resolved shear stress factor given by $s = \cos \lambda \cos \varphi$ where λ is the angle between specimen axis and normal to the

slip plane and φ the angle between specimen axis and slip direction. $\Omega = (E/G) \sum_i (A_i/A) s_i^2$ and $\sum_i A_i = A$, where quantities with suffix i belong to the i th slip system. A is dislocation density in the specimen, L_n loop length of the dislocation network, L_c mean distance between point defects on the dislocation line, F the maximum binding force between the point defect and dislocation, and B damping constant for dislocation movement. The value of L_c takes the exponential distribution in the present case, while L_n is assumed to be constant throughout a specimen.

3.3 Dislocation damping in quartz

Although the crystal of quartz is not as ductile as usual metals, there are some facts which suggest the presence of dislocations in this material. Frederickson¹³⁾ observed a mosaic structure developed by etching, which was usually indicative of the presence of dislocations. Keymeulen¹⁴⁾ revealed dislocation lines decorated with silver atoms using a special technique. Noggle *et al.*¹⁵⁾ determined the dislocation density in single crystals of quartz with high-resolution X-ray diffraction methods.

There are further some indications of dislocation damping in quartz crystals. The frequency of quartz resonator was sometimes found to decrease with increasing strain amplitude¹⁶⁾. Such behavior is assumed to be originated from the non-linear properties of the vibrating dislocations. The small residual aging of the elastic properties of quartz after processing the crystal, which is observed as the long-time change of frequency¹⁷⁾, is probably due to the stabilization of dislocations in the crystal. Mason analyzed the low-temperature relaxation peak appeared in quartz crystal, and found that the Peierls' stress for the dislocation in quartz was smaller than those for usual metals¹⁸⁾. If it is the case, dislocations may be the cause of the room-temperature internal friction in quartz because they can vibrate rather easily under the influence of the external alternating stress.

In the following section, the experimental results obtained by the present investigation will be analyzed with the theory described in section 3.2, although it may be somewhat uncertain to apply the theory for the internal friction of quartz crystals.

3.4. Analysis of the results

The amplitude-dependent part of the internal friction $\delta_h = \delta - \delta_i$ is extracted from Fig. 2, where δ_i is obtained by extrapolating the value of δ to $\varepsilon=0$. In Fig. 4, values of $\log \varepsilon^{1/2} \delta_h$ are plotted against ε^{-1} for several specimens. It is found that linear relationship holds between these two variables, as Eq. (2) requires. The values of c_0 and c_1 in Eq. (2) can be determined by the intercept and the slope of the straight line. The same

plot for the anomalous specimen 'H' is composed of two straight lines with different slopes, as shown in Fig. 5. The values of δ_i , c_0 and c_1^{-1} thus determined for various specimens are represented in Figs. 6, 7 and 8, where the abscissae are the angle θ . The values of c_0 and c_1 for the specimens parallel to Y- or Z-axis cannot be determined.

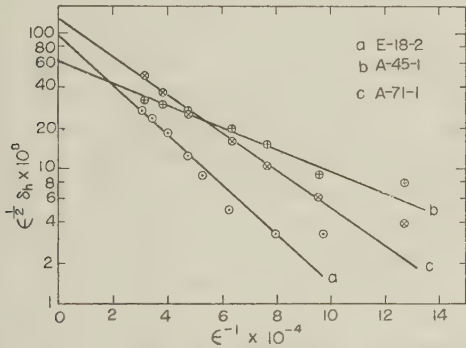


Fig. 4. Analysis of amplitude dependence of internal friction for various specimens.

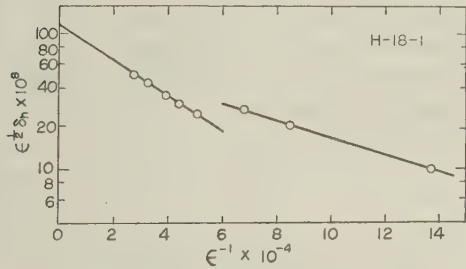


Fig. 5. Analysis of amplitude dependence of internal friction for specimen 'H'.

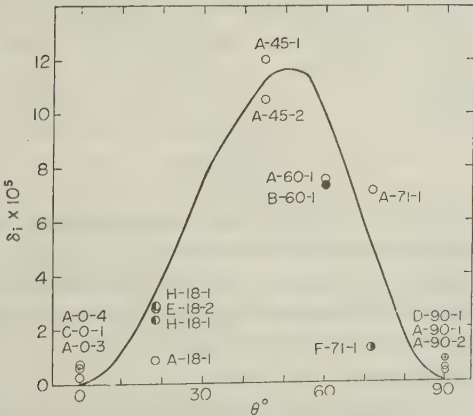


Fig. 6. Values of δ_i for various specimens.

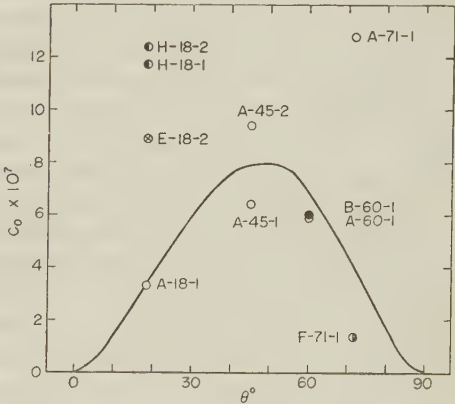


Fig. 7. Values of c_0 for various specimens.

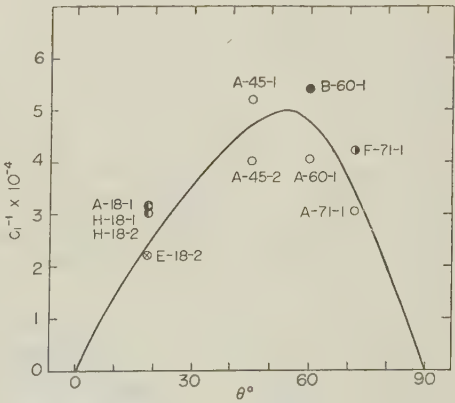


Fig. 8. Values of c_1^{-1} for various specimens.

For specimens 'H', the lines with larger slopes were used to determine c_0 and c_1 . It can be obviously seen that these three quantities are dependent on the crystallographic orientation of the specimen. These facts can be explained by the above theory described in section 3.2. Of all factors which determine δ_i , c_0 and c_1 , the Young's modulus E , the orientation factor $\mathcal{Q}$ and the resolved shear stress factor s are dependent on the orientation of the specimen. If A , L_c and L_n are not different in each specimen, the orientation dependences of the above quantities can be expressed as

$$\left. \begin{aligned} \delta_i &= K_1 s^2 E, \\ c_0 &= K_2 \sqrt{s^3 E}, \\ c_1^{-1} &= K_3 s E, \end{aligned} \right\} \quad (3)$$

where K_1 , K_2 and K_3 are independent of the orientation. It can be shown from a geometrical consideration that only when the dislocations in the crystal have the slip plane parallel to Y- or Z-axis, the resolved shear stress factor $s=0$ for $\theta=0$ or 90° while $s \neq 0$ for $\theta \neq 0$ or 90° . In these cases, the factor can be expressed as $s = K_4 \sin \theta \cos \theta$, where K_4 is a constant related to the actual slip direction. Inserting this into Eq. (3), three quantities can be calculated as functions of θ . They are shown as the solid curves in Figs. 6, 7 and 8, respectively. These curves are normalized so as to pass the midpoints of the two experimental points for A-45-1 and A-45-2. The agreements of these curves with experimental results are considered to be satisfactory, since the dislocation density and the concentration of impurities may vary from specimen to specimen.

3.5. Effects of annealing

The internal friction of a specimen A-45-1, annealed at 500°C for 20, 50, 100 and 150 hours successively, was measured as a function of the strain amplitude for each state during annealing. The relative values of A , L_n and L_o^{-1} can be calculated from Eqs. (1) and (2) by eliminating the unknown quantities F and B . The variations of these three quantities with annealing time are shown in Fig. 9, where the values of A , L_n and L_o^{-1} of the specimen annealed for 150 hours are chosen to be unities. It is found that, as the specimen is annealed, the dislocation density,

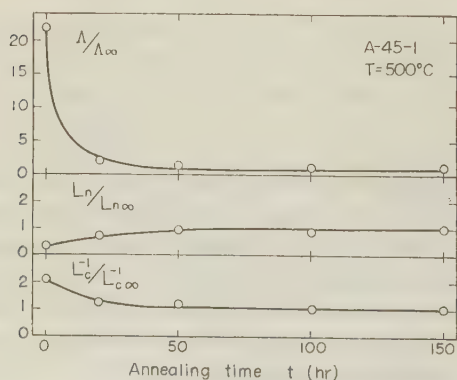


Fig. 9. Variations of A , L_n and L_o^{-1} of a specimen annealed at 500°C .

A , decreases greatly, and the network length, L_n , increases slightly. Annealing the specimen at 500°C may cause the annihilation of unstable dislocations, since the natural quartz is assumed to have grown at temperatures lower than 350°C under the ground¹⁹⁾. The number of the pinning points on the dislocation, which is proportional to L_o^{-1} , seems to decrease apparently as the specimen is annealed. This phenomenon may be explained when the knowledges about the nature and kind of the pinning defects are obtained.

3.6. Estimation of dislocation density

In order to estimate the dislocation density from the present experimental data, the preferable slip system of the dislocation in the quartz crystal must be discussed first. It has been shown in section 3.4 that the dislocations which contribute to the internal friction have the slip plane parallel to Y- or Z-axis. Considering the atomic configuration in the crystal, dislocation lines may lie along $[10.0]$ direction and the slip plane may be either (10.0) plane (m -plane) or (00.1) plane (Z -plane). It can be further presumed that the most probable slip system is $[01.0]/(00.1)$, since dislocations with such system have the minimum self energy²⁰⁾. In such a case, the resolved shear stress factor and the orientation factor are expressed as $s = (\sqrt{3}/2) \sin \theta \cos \theta$ and $\varrho = (E/G)(2s^2/3)$, and the Burgers vector equals to the length of the unit cell a_0 ($\approx 4.91\text{\AA}$).

In Eqs. (1) and (2), the unknown factors are A , L_n , L_o , F and B , while δ_i , c_0 and c_1 can be determined experimentally and all others are known quantities. Among the five unknown factors, the damping constant, B , will be calculated by Leibfried's formula²¹⁾, although it can give the correct value only in order of magnitude¹²⁾. This is given by

$$B = \frac{3zkT}{10v_s a^2}, \quad (4)$$

where z is the number of atoms per unit cell, v_s the velocity of shear waves in the crystal, a the lattice parameter and k is Boltzmann's constant. The value of B for quartz at room temperature is thus calculated to be 4.0×10^{-5} gr/cm. sec.

For a specimen, A-45-1, annealed at 500°C for 150 hours, the dislocation density in the

Table II.

L_n cm	L_o cm	A cm ⁻²	F dyne	b/L_o
5×10^{-5}	6.0×10^{-6}	2.9×10^6	3.8×10^{-5}	8.2×10^{-4}
1×10^{-4}	9.0×10^{-6}	5.6×10^5	5.7×10^{-6}	5.5×10^{-4}
5×10^{-4}	1.4×10^{-4}	1.2×10^4	1.5×10^{-4}	2.0×10^{-4}
1×10^{-3}	3.6×10^{-4}	2.3×10^3	2.3×10^{-4}	1.4×10^{-4}

crystal will be estimated. Inserting the above value of B into Eq. (1), and regarding L_n as a parameter, the values of L_o , A and F can be calculated. The results are listed in Table II, where the concentration of the pinning points on the dislocation line, b/L_o , are also shown. Considering the pinned-down model of dislocations used to derive Eqs. (1) and (2), the inequality, $L_n/L_o - 1 > 1$, must always hold. From this restriction, the following relation is obtained: $L_n > 4 \times 10^{-4}$ cm. Etching experiments about quartz crystals¹³⁾ have shown that the size of the mosaics, which is considered to correspond to L_n mentioned above, is $10^{-4} - 10^{-3}$ cm. Thus the most probable value of L_n to be adopted in the present case may be $L_n = 5 \times 10^{-4} - 10^{-3}$ cm. Then the following values are obtained for the specimen: $L_o = 2 - 4 \times 10^{-4}$ cm, $A = 3 \times 10^3 - 1 \times 10^4$ cm⁻² and $F = 1 - 3 \times 10^{-4}$ dyne.

Mason⁵⁾ estimated the dislocation density in quartz to be 10^3 cm⁻² through analyzing the low-temperature relaxation peak, while the value determined by X-ray methods¹⁵⁾ has been $10^5 - 10^6$ cm⁻².

3.7. Defects pinning dislocations

The theory adopted above assumes that the dislocations are pinned down by point defects which exert forces on the dislocation lines. The pinning defects in metals are usually considered to be impurity atoms or vacancies. In natural crystals of quartz, metallic impurities such as Al, Fe, Mg, Ca, Li, Na and K are usually contained. Some of these impurities may interact with dislocations and pin them down. In the present experiment, the concentrations of the pinning points on the dislocation line, $C = b/L_o = \pi b^2 s E c_1 / 2F$, can be calculated and these values for specimens 'A', 'F' and 'H' are shown in Table III, where F is chosen to be 10^{-4} dyne. It is found that the concentrations for three kinds of specimens are not different. The pinning defects are presumed to be associated with Na,

since the contents of Na in three crystals are rather large and nearly alike [Table I]. Alkali ions in quartz can move rapidly, and some of them may be gathered to the dislocation lines and act as pinning points. Although Al and K are also contained commonly in three crystals, their contents are different considerably. The anomalous behavior of the specimen 'H' observed in the internal friction *vs* strain amplitude curve [Fig. 3] may be due to K atoms, since the crystal contains large amount of K compared

Table III.

Specimen	$c_1 \times 10^5$	$sE \times 10^{-12}$	$C \times 10^4$
A-18-1	2.96	0.184	2.06
A-45-1	1.85	0.361	2.53
A-45-2	2.47	0.361	3.38
A-60-1	2.43	0.366	3.37
A-71-1	3.23	0.266	3.26
F-71-1	2.25	0.266	2.27
H-18-1	3.02	0.184	2.10
H-18-2	3.27	0.184	2.28

with other crystals. When a specimen contains effective pinning defects of two kinds, the plot of $\log \epsilon^{1/2} \delta_h$ *vs* ϵ^{-1} may be composed of two straight lines with different slopes, because the values of c_1 may be different for different kinds of defects. This expectation is considered to be fulfilled as shown in Fig. 5.

In general, point defect interacts with dislocation line through the Cottrell mechanism. In the case of quartz crystal, the maximum binding force between a dislocation line and a Na atom on it, calculated by the Cottrell's formula, is of the order of 10^{-6} dyne. This disagrees in order of magnitude with the value, $F = 10^{-4}$ dyne, obtained through analyzing the results of the internal friction measurement [section 3.6]. In some cases, the values of F evaluated by the internal

friction method are found to be 10-20 times the values given by the Cottrell mechanism^{11), 22)}. Koehler²²⁾ suggested that these discrepancies may occur when more than one point defect occupy a pinning point, or atomic size is not the important source of binding between point defect and dislocation. The following is a proposition to explain the above discrepancy which is more serious in the present case. Assume that there are widely spaced aggregates of impurities such as Na or K in the vicinity of the dislocation lines, although these aggregates are not confirmed to exist through other experimental methods. Dislocation line between network pinning points bows out when an external stress is applied. The dislocation line is obstructed by the aggregates that intersect the slip plane. As the applied stress is further increased, the dislocation line finally breaks away from the obstacles, leaving a trapped small dislocation loop around each of them. This mechanism of the 'by-passing' of obstacles by dislocation line has been proposed by Orowan to explain the slip in over-aged alloys. Some work is necessary to form the small dislocation loop when the dislocation line escapes from the obstacle. As the external stress is decreased, the dislocation line returns to the original position, and the trapped dislocation loops disappear when they meet with the dislocation line. Accordingly, such aggregates are able to act as breakable pinning points through mechanism described above when they are composed of impurity atoms fewer than about one hundred, since the maximum displacement of the dislocation line between pinning points is about $5b$ when $L_0 = 3 \times 10^{-4}$ cm and $\varepsilon = 10^{-6}$. Fisher *et al.*²³⁾ considered the 'by-passing' mechanism and calculated the energy, E , to form the closed dislocation loop around a particle with circular cross-section of radius r . Their result showed that $E \approx (3/4)Gb^2r$. The maximum interaction force between a dislocation line and such an obstacle, f , is considered to be nearly equal to $E/2r$. In the case of quartz crystal, it becomes that $f \approx (3/8)Gb^2 = 4 \times 10^{-4}$ dyne. This value agrees in order of magnitude with the value of F obtained in section 3.6.

Acknowledgement

The author wishes to express his sincere gratitudes to Dr. T. Kawada for his continued encouragement. He is also greatly indebted to Professor Y. Tomono for his advice. Thanks are also due to Mr. K. Takahashi at the Geological Survey of Japan for his kindness to carry out the spectroscopic analysis of the specimens.

References

- 1) R. A. Artman: J. Appl. Phys. **23** (1952) 475.
- 2) G. A. Alers: J. Appl. Phys. **24** (1953) 324.
- 3) R. K. Cook and R. G. Breckenridge: Phys. Rev. **92** (1953) 1419. R. K. Cook and J. H. Wasilik: J. Appl. Phys. **27** (1956) 836.
- 4) J. H. Wasilik: Phys. Rev. **105** (1957) 1174.
- 5) H. E. Bömmel, W. P. Mason and A. W. Warner: Phys. Rev. **99** (1955) 1894, **102** (1956) 64.
- 6) J. C. King: Phys. Rev. **109** (1958) 1552; Bell Sys. Tech. J. **38** (1959) 573.
- 7) D. L. White: J. Appl. Phys. **29** (1958) 856.
- 8) E. R. Fitzgerald: Phys. Rev. **112** (1958) 765.
- 9) J. Marx: Rev. Sci. Instr. **22** (1951) 503.
- 10) Y. Hiki: J. Phys. Soc. Japan **13** (1958) 1138.
- 11) A. Granato and K. Lücke: J. Appl. Phys. **27** (1956) 583, 789. K. Lücke and A. Granato: *Dislocations and Mechanical Properties of Crystals* (John Wiley and Sons, Inc., New York, 1957) 425.
- 12) Y. Hiki: J. Phys. Soc. Japan **14** (1959) 590.
- 13) A. F. Frederickson: Amer. Mineral. **40** (1955) 1.
- 14) J. van Keymeulen: Naturwiss. **44** (1957) 489.
- 15) T. S. Noggle and J. S. Koehler: Acta Met. **3** (1955) 260.
- 16) A. R. d'Heedene: *Quartz Crystals for Electrical Circuits* (R. A. Heising Editor, D. Van Nostrand Co. Inc., Princeton, 1946) 456.
- 17) H. T. Mitchell: Nature **174** (1954) 41.
- 18) W. P. Mason: *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Co. Inc., Princeton, 1958) 271.
- 19) H. S. Scott: Econ. Geol. **43** (1948) 637.
- 20) H. Iwasaki: private communication.
- 21) G. Leibfried: Z. Phys. **127** (1950) 344.
- 22) J. S. Koehler: *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952) 197.
- 23) J. C. Fisher, E. W. Hart and R. H. Pry: Acta Met. **1** (1953) 336.

Interaction of Exciton with Electron Trapping Centers in Alkali Halide Crystals.

2. Quantum Yield for the $U \rightarrow F$ Conversion and Its Dependence on U -Center Concentration

By Masayasu UETA, Masamitsu HIRAI
and Hiroyuki WATANABE

*Department of Physics, The Faculty of Science,
University of Tohoku, Sendai*

(Received November 20, 1959)

The quantum yield for the photochemical conversion of a U center to an F center as a function of illuminating photon energy has been investigated in KCl, KBr and their mixed crystals. For photons in the U -absorption band the yield increases with the illuminating photon energy. It has been determined that the conversion occurs with a maximum yield of nearly unity for photons both in the shorter wavelength tail of the U -absorption band and in the fundamental absorption tail-exciton band. The dependence of the yield of exciton-induced $U \rightarrow F$ conversion upon the temperature and U center concentration has also been studied. The yield of unity is independent of the concentration in the range higher than $1.0 \times 10^{17}/\text{c.c.}$; however, it drops appreciably below $5 \times 10^{16}/\text{c.c.}$, indicating that the exciton is movable and its maximum length of migration is of the order of $3 \times 10^{-6} \text{ cm}$.

§ 1. Introduction

U centers can be converted from F centers when alkali halide crystals additively colored are heated in a hydrogen atmosphere, and display a bell shaped optical absorption band in the ultra violet region, with maximum absorption at $\lambda\lambda$ 228 $m\mu$ and 216 $m\mu$ in KBr and KCl crystals, respectively, at room temperature.

The properties of U centers have been extensively studied by Hilsch and Pohl¹⁾ and a model of an H^- ion occupying substitutionally the position of a halogen ion has been given for it.

At high temperature (above -100°C) in the case of the KBr crystal, U centers are converted photochemically to F centers with ultra violet light in its absorption band. The quantum efficiency is about 30 percent at room temperature when the crystal is irradiated by light at the U -absorption peak. The temperature dependence of the yield has been measured by Hilsch and it is explained by Mott and Gurney²⁾ using the configurational coordinate diagram.

U centers can also be converted to F centers by irradiating the crystal containing the hydride with X-rays at room temperature.

Pick and Martienssen³⁾ observed that the rate of F center production is much faster and F centers thus produced are relatively more stable than those generated by X-rays in pure salt. They have determined the value of 35 eV for the initial energy required to convert a U center to an F center in a KBr crystal. In KCl crystal, we have obtained nearly the same value as will be reported elsewhere.

On the conversion of $U \rightarrow F$ by X-rays, Seitz⁴⁾ has proposed that an electron-hole pair is generated by X-rays, the hole may annihilate an electron of a U center and the hydrogen atom may diffuse away from the vacancy and be replaced by an electron.

He has also pointed out that there might be other processes of ionization or excitation of U centers by an exciton, but he concluded that these processes will not be predominant, because the quantum yield of $U \rightarrow F$ conversion by a U light in a KCl crystal will be smaller than 20 percent in the case of KBr crystal and at least 7 eV is required to produce an exciton, therefore, the minimum energy required to convert a U center to an F center should be much larger than the 35 eV which was determined experimentally.

Moreover, Seitz has pointed out that it

would be very interesting to examine the quantum yield for the conversion with photons in the tail of the fundamental absorption band-exciton absorption band-because it would provide convincing evidence of the exciton migration, if the efficiency is the same as for photons absorbed in the U band.

If the quantum yield of $U \rightarrow F$ conversion by light in the U absorption band increases instead of remaining constant as the energy of the irradiating photon does, the minimum energy required to convert a U center to an F center by X-rays might be smaller than 35 eV. Therefore, the reason for rejecting the possibility of processes of ionization or excitation of U centers by the exciton will not exist.

Measurements of the quantum yield by photons in the U absorption band as a function of illuminating photon energy and by photons in the fundamental absorption tail are thus important.

In a previous report⁵⁾ it has been observed that the quantum efficiency increases more when the wavelength of illuminating light was decreased below the U absorption peak and has a maximum value at the position where the fundamental absorption tail and U -absorption band are superimposed.

We determined the quantum efficiency with light of the U -absorption peak to be 45 percent and the maximum yield was more than unity. This was found to be due to the over-estimation of the yield value of 18 percent with light of λ 253 $m\mu$. After careful measurements it was determined to be 12 percent at room temperature. Therefore, the quantum yield at the U -absorption peak became 30 percent, in agreement with Hilsch's values, and the maximum efficiency was nearly unity.

In the present report a more detailed determination of the absolute quantum yield and its dependence upon both temperature and U center concentration will be described.

§ 2. Experimental Procedure

U centers were prepared in KBr and KCl crystals of the Harshaw Chemical Co. by heating the crystals containing F centers at 540°C in a hydrogen atmosphere at high pressure. Almost all F centers existing initially are converted to U centers by this procedure.

The concentration of U centers $[U]$ in the

KBr crystal can be calculated by the following formula given by Hilsch⁶⁾;

$$[U] = 5.1 \times 10^{16} \times f_{\lambda} \times K_{\lambda}$$

at room temperature,

where K_{λ} is the absorption coefficient meas-

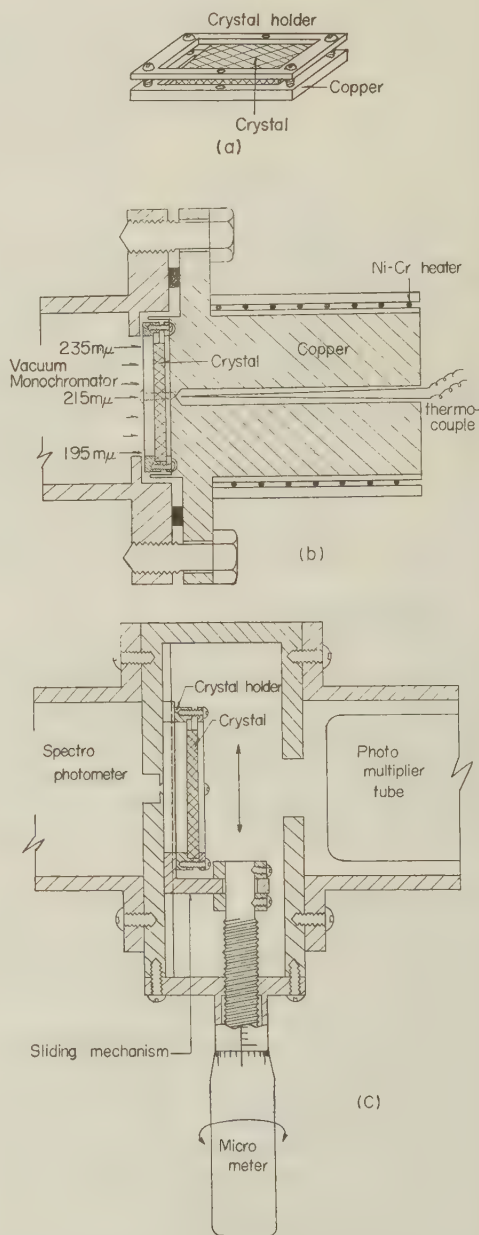


Fig. 1. (a) Crystal holder. (b) Mounting of the crystal to be illuminated by the ultraviolet light. (c) Schematic diagram of the measurement of the density distribution of F centers. Transmission at F absorption peak of the illuminated crystal is measured from one end to the other continuously by the sliding mechanism which is driven by a micrometer screw.

ured in mm^{-1} and the f_λ 's are constants depending on the wavelength of the light with which the absorption coefficients of the U band are measured, and have the following values:

($m\mu$)	Absorp. peak 228	Hg. 245	Hg. 254	Cd. 257	Hg. 265
f_λ	1	8	21.2	43.2	235

A KBr crystal containing U centers was cleaved to the dimension of $20 \times 10 \times 3 \text{ mm}^3$ and mounted on the crystal holder which is shown in Fig. 1(a). The crystal holder was fixed on the focal plane of the powerful vacuum monochromator* as shown in Fig. 1(b) in such a manner that the crystal surface of $20 \times 10 \text{ mm}^2$ can be irradiated by light of continuous spectrum from the hydrogen discharge tube. Crystals can be warmed by conduction from the Ni-Cr heater.

The width of an entrance slit of the monochromator is 1 mm and the dispersion is $2 \text{ m}\mu/\text{mm}$ at the focal plane. Therefore, when the midpoint of the crystal surface is set to be illuminated by a certain monochromatic light, for example of $215 \text{ m}\mu$, the surface of the crystal is illuminated with continuous light ranging from $195 \text{ m}\mu$ to $235 \text{ m}\mu$. In the crystal, $U \rightarrow F$ conversion occurs after the illumination, but the number of F centers thus generated is not uniform but depends on both the intensity distribution of the continuous spectrum and the quantum yield.

The crystal holder was removed from the monochromator after illumination and set at the exit slit of the spectrophotometer to measure the transmission continuously from one end to the other of the crystal after it was fixed on the sliding mechanism having a micrometer screw as shown in Fig. 1(c). From the measurements of transmission (I/I_0

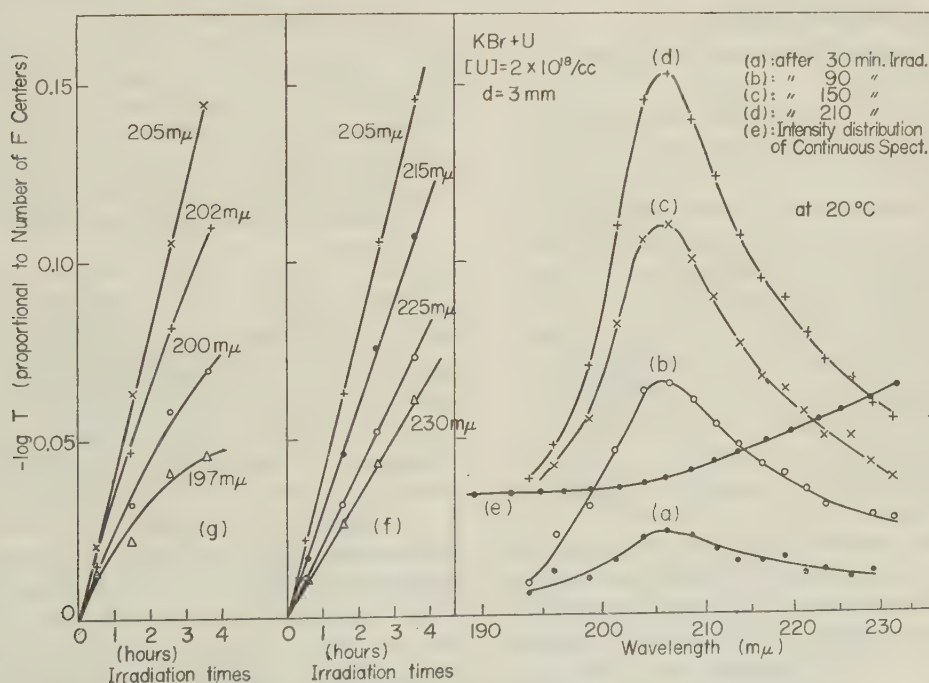


Fig. 2. Spectral density variation of F centers converted from U centers in a KBr crystal at 20°C . Curves (a), (b), (c) and (d) show the number of F centers generated after 30, 90, 150 and 210 minutes' illumination, respectively.

Curve (e) shows the spectral intensity distribution of the hydrogen discharge light source at the focal plane of the vacuum monochromator.

Straight lines of (f) indicate that F centers are produced linearly with illuminating times with wavelengths longer than $205 \text{ m}\mu$. Curve (g) shows the saturation of F center-generation for wavelengths shorter than $205 \text{ m}\mu$.

* The details of the vacuum monochromator has been described in the previous report⁽⁵⁾.

at the wavelength of the F absorption peak) the number of generated F centers can be calculated by the well known Smakula equation:

$$n_0 f = 1.31 \times 10^{17} \frac{n}{(n^2 + 2)^2} \cdot \alpha_m \cdot H, \quad (\text{KBr})$$

putting $n=1.53$, $H=0.36$ (eV) and $f=0.85$, where n is the index of refraction of the KBr crystal at the F -absorption peak, α_m and H the absorption coefficient in cm^{-1} and the half value width of the F -band in electron volt, respectively. f is the oscillator strength.

The relative intensity distribution of the continuous spectrum of light at the focal plane of the vacuum monochromator was obtained by measuring the intensities of fluorescence impressed on the film of sodium salicylate, because the fluorescent film is found⁷⁾ to have the same quantum efficiency to monochromatic light from 300 $\text{m}\mu$ down to 100 $\text{m}\mu$.

§ 3. Experimental Results

3.1 Dependence of quantum yield upon photon energy

The result in the KBr crystal containing U centers with a concentration of $2 \times 10^{18}/\text{c.c.}$ is shown in Fig. 2. Curve (a) is the relation of the number of F centers converted from U centers after the 30 minutes' irradiation as a function of illuminating photon energy. Curves (b), (c) and (d) are the same relations after 90, 150 and 210 minutes' irradiation, respectively. Curve (e) is the relative intensity distribution of the continuous spectrum of the hydrogen discharge tube at the exit slit of the monochromator.

For the illumination wavelength longer than 205 $\text{m}\mu$, the number of generated F centers is linearly proportional to the irradiation time and there is no saturation within 210 minutes. The straight lines on the left side of Fig. 2 shows the linear relations clearly. Therefore, the number of F centers indicates the relative quantum yield of $U \rightarrow F$ conversion if it is corrected by the intensity distribution of the continuous light.

The absolute quantum yield using monochromatic light of Hg 253 $\text{m}\mu$ has been found to have a value of 0.12 through measurements of the number of photons and the number of generated F centers. Using this value of 0.12 as the standard, we can determine the

absolute quantum yield as a function of the photon energy of the illuminating light.

Curve (a) of Fig. 3 shows the absolute quantum yield thus obtained in the region of wavelength longer than 205 $\text{m}\mu$. As seen from the figure, the maximum yield is very close to unity and at the U -absorption peak it has a value of about 28 percent, which coincides with that of Hilsch. Curve (b) in Fig. 3 indicates the absorption coefficients of

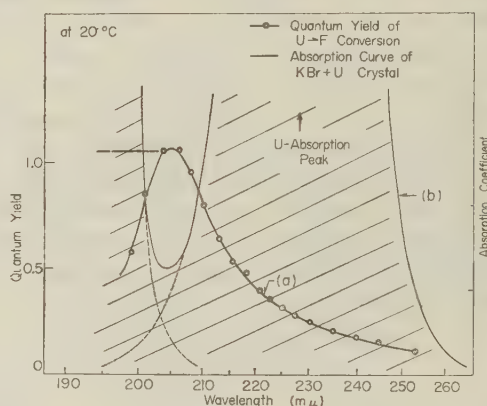


Fig. 3. (a) Variation of quantum yield for the reaction $U \rightarrow F$ in KBr crystals as a function of illuminating photon energy at 20°C. The drop of yield below 205 $\text{m}\mu$ is due to the F center saturation. Real yield variation is indicated by the dotted line. (b) Absorption curve of KBr + U crystal.

the KBr + U crystal. The absorption coefficient of the crystal of 3 mm thickness is so high in the whole wavelength range of measurement that the absorption curve was obtained in a thin cleaved crystal of 0.2 mm thickness. In the wavelength region between 190 $\text{m}\mu$ and 255 $\text{m}\mu$, a crystal of 3 mm thickness containing U centers with a concentration as high as $10^{18}/\text{c.c.}$ is quite opaque and all incident photons are absorbed in the crystal. Therefore, it is unnecessary to make the correction against the spectral variation of absorption. Furthermore, consideration of the reflectivity change with the wavelength of light has been neglected, because it should have a uniform value as the U center concentration is much smaller than that of the constituents of the host crystal.

The wavelength side of curve (a) in Fig. 3 shorter than 205 $\text{m}\mu$ does not indicate a true quantum yield of $U \rightarrow F$ conversion, because in this exciton absorption region the number

of generated F centers saturates. This is due to the fact that the penetration depth of light into the crystal is small and the back reaction of $F \rightarrow U$ conversion occurs.

The number of F centers generated by each light of λ 202, 200 and 197 $m\mu$ is plotted against the irradiation time as shown in Fig. 3 (g). The slope of the curve for the λ 202 $m\mu$ coincides with the straight line for the λ 205 $m\mu$. Slopes of curves for lights of λ 202 $m\mu$ and 197 $m\mu$ do not coincide with 205 $m\mu$, but if we take account of the decrease of light intensities for these wavelengths, it is seen that they are the same as that for λ 205 $m\mu$. Therefore, it may be concluded that the absolute quantum yields in the region shorter than λ 205 $m\mu$ are also very close to unity as shown by the dotted circles in Fig. 3 (a).

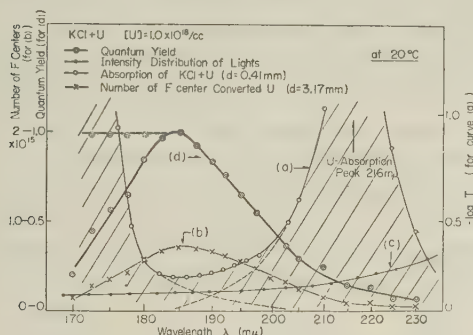


Fig. 4. Spectral variation of the quantum yield for $U \rightarrow F$ conversion in a KCl crystal at 20°C.

(a) Absorption curve of a KCl+ U crystal of 0.41 mm thickness.

(b) Spectral distribution of F center densities after 125 minutes' illumination.

(c) Spectral intensity distribution of light.

(d) Absolute quantum yield as a function of photon energy.

In a KCl crystal containing U centers with a concentration of $1.0 \times 10^{18}/c.c.$, similar measurements were carried out at room temperature. The result is shown in Fig. 4. The absorption curve of a KCl+ U crystal has been measured with a thin crystal of 0.41 mm thickness as shown in curve (a). The distribution of F center density generated from U centers as a function of photon energy after 125 minutes' irradiation is shown by the curve (b). In this case the number of F centers also increases linearly with an irradiation time if the wavelengths of light are longer than 183 $m\mu$ as indicated in Fig. 5 (a). Therefore,

the variation of F center density itself gives the relative quantum yield of $U \rightarrow F$ conversion, if they are corrected by the spectral intensity distribution of light as shown by the curve (c).

For light shorter than λ 183 $m\mu$, the penetration depth into the crystal is small and the saturation of $U \rightarrow F$ conversion occurs as shown in Fig. 5 (b). However, if we plot the initial slope of the F center growth the quantum yield is considered to be the same as that for light of λ 183 $m\mu$.

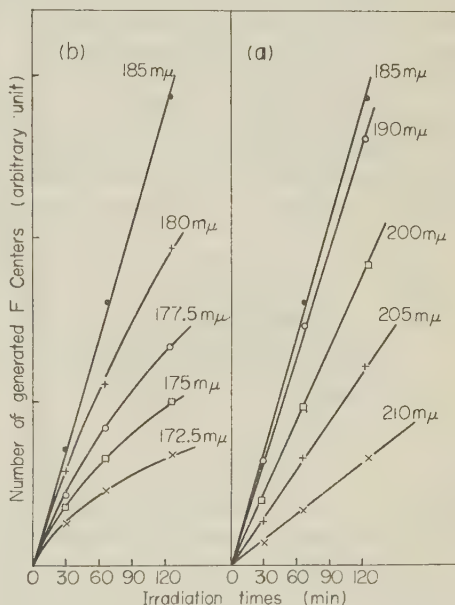


Fig. 5. Relation between F center generation and illuminating time.

(a) The linearity exists for light longer than λ 185 $m\mu$.

(b) Saturation of F center generation for light shorter than λ 185 $m\mu$.

The absolute light intensity below λ 220 $m\mu$ is too weak to be measured with a thermopile, therefore, to obtain the absolute quantum yield in KCl crystals, the following procedure was applied. A KCl+ U crystal and a KBr+ U crystal were held together side by side in the crystal holder shown in Fig. 1 in such a manner that the KCl and KBr crystals can be illuminated with light ranging from 180 $m\mu$ to 200 $m\mu$ and from 200 $m\mu$ to 220 $m\mu$, respectively, at the focal plane of the vacuum monochromator. After the irradiation of proper period, the number of F centers created from U centers were measured as described

before. The result is shown in Fig. 6. Curve (a) is the distribution of F center density and curve (b) is a spectral intensity distribution of light. With light of λ 205 $m\mu$, F centers can be converted from U centers with a quantum yield of unity in KBr crystals as determined before. From these figures it was found that with light of λ 185 $m\mu$, F centers are converted from U centers with a quantum yield of nearly unity in KCl crystal too. Curve (c) is the absolute quantum yield thus determined. From the quantum yield of unity in KCl crystal at λ 185 $m\mu$, we can plot the curve of the absolute quantum yield as a function of light energy as shown by the curve (d) in Fig. 4.

In mixed crystals of KCl(75%)+KBr(25%) and KCl(50%)+KBr(50%) the same types of spectral variation of the quantum yield for the $U \rightarrow F$ conversion have been measured.

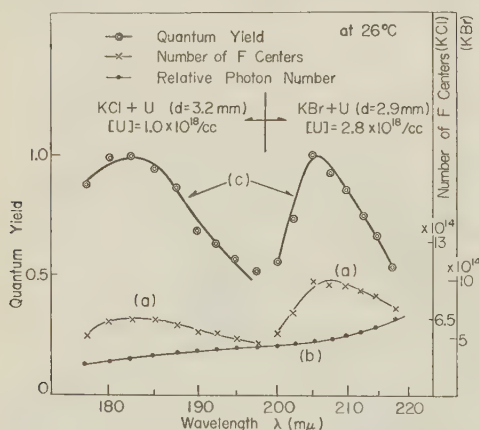


Fig. 6. Determination of absolute quantum yield in a KCl crystal.

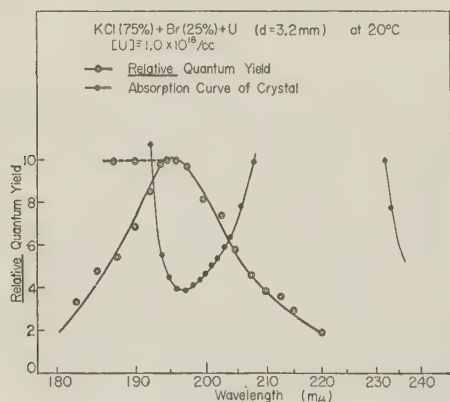


Fig. 7. Spectral variation of the relative quantum yield for the reaction $U \rightarrow F$ in the mixed crystal of KCl and KBr.

Fig. 7 shows the relative yield in one of the mixed crystals. In all cases of KCl, KBr and their mixed crystals the quantum yield reaches a maximum value at the position in the fundamental absorption tail where the absorption coefficient is increasing steeply, and in KCl and KBr crystals the maximum value is nearly unity.

3.2 Temperature dependence of quantum yield

The temperature dependence of the quantum yield for the photochemical reaction of $U \rightarrow F$ conversion in KBr crystals with light of U -absorption peak has been measured by Hilsch¹¹ as shown in Fig. 8 and the yields are about 0.45 and 0.60 at 100°C and 150°C, respectively.

The spectral variations of the quantum yield at 100°C and 150°C were measured with the same procedure as before and the results shown in Fig. 9 were obtained. In the figure, maximum yield values are normalized to unity. At the peak of the U -absorption band, yield values are 0.4 and 0.5 at 100°C and 150°C,

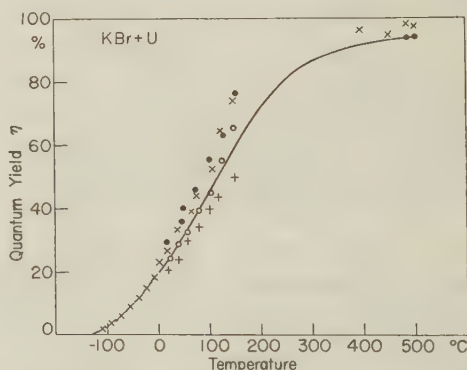


Fig. 8. Temperature dependence of quantum yield in KBr Crystals with light of U absorption peak (by Hilsch).

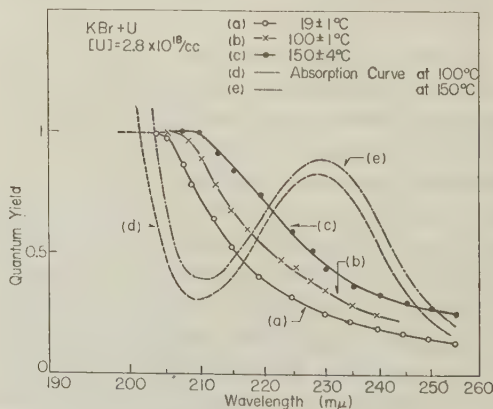


Fig. 9. Spectral distribution of quantum yield at 20°C, 100°C and 150°C.

respectively. These values are a bit smaller than the mean value of Hilsch's observation but coincide well with that of the specimen indicated by (+) in Fig. 8.

From these facts it may be concluded that the quantum yield increases with the temperature for light in the *U*-absorption band. However, for light in the region of the fundamental absorption band, it does not depend on temperature over the range from room temperature to 150°C but has a constant value of unity.

3.3 Dependence of quantum yield upon the *U*-center concentration

From the results obtained above, it has been concluded that the ultra violet light in the fundamental absorption band can convert a *U* center to an *F* center with a quantum yield of unity. On the other hand, it is well known that when the alkali halide crystals absorb light in their first fundamental absorption band, an exciton is generated.

However, the mechanism of how the energy of the exciton is transferred to *F* center or other electron trapping or luminescent centers is not clear yet. The investigation of the quantum yield as a function of the concentration of these centers will shed some light on this problem.

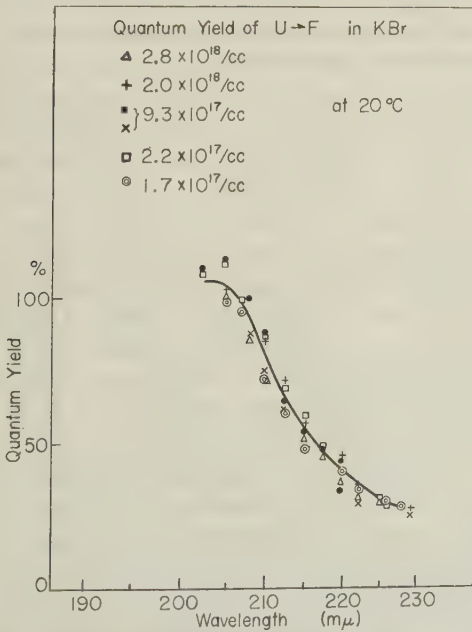


Fig. 10. Independence of quantum yield upon the *U* center concentration in the range from 1.7×10^{17} to 2.8×10^{18} /c.c.

Similar measurements of the quantum yield in KBr crystals containing *U* centers in the concentration range from 1.7×10^{17} to 2.8×10^{18} per cubic centimeters were carried out at room tempertaure. The results are shown in Fig. 10. The spectral variations of the yield are the same for all crystals within the experimental error of 15 percent. Therefore, the conclusion of the concentration independence will be deduced. However, if the *U* center concentration is as low as 2.6×10^{16} /c.c., the yield drops appreciably in the fundamental absorption region as described below.

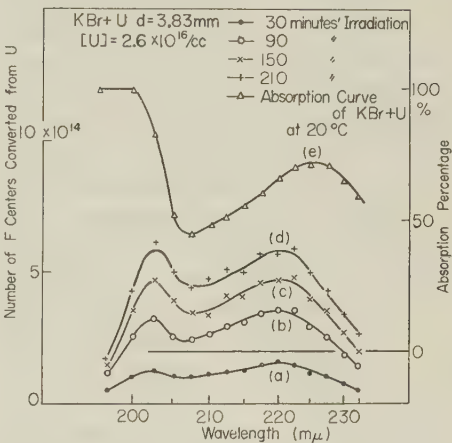


Fig. 11. Spectral variation of *F* center density converted from *U* centers in KBr crystal containing a small *U* center concentration of 2.6×10^{16} /c.c. Curves (a)–(d) show the *F* center densities after 30, 90, 150 and 210 minutes' illumination, respectively. Curve (e): Absorption curve of the crystal (%).

Curves (a)–(d) in Fig. 11 show the spectral variation of *F* center generation after successive periods of illumination of 30, 90, 150 and 210 minutes, respectively. Curve (e) shows the absorption percentage of the KBr+*U* crystal of 3.83 mm thickness. As the concentration of *U* centers is small, the growth rate of *F* centers is not linear to the illumination time but tends to saturate in the whole spectral range. Therefore, to obtain the variation of quantum yield we plotted curves showing the number of *F* centers versus illumination time and measured the slopes at zero illumination as shown in Fig. 12. The relative quantum yield thus obtained is shown in Fig. 13(a). To obtain a true quantum yield η , this curve was corrected for both the spectral intensity distribution of light and the

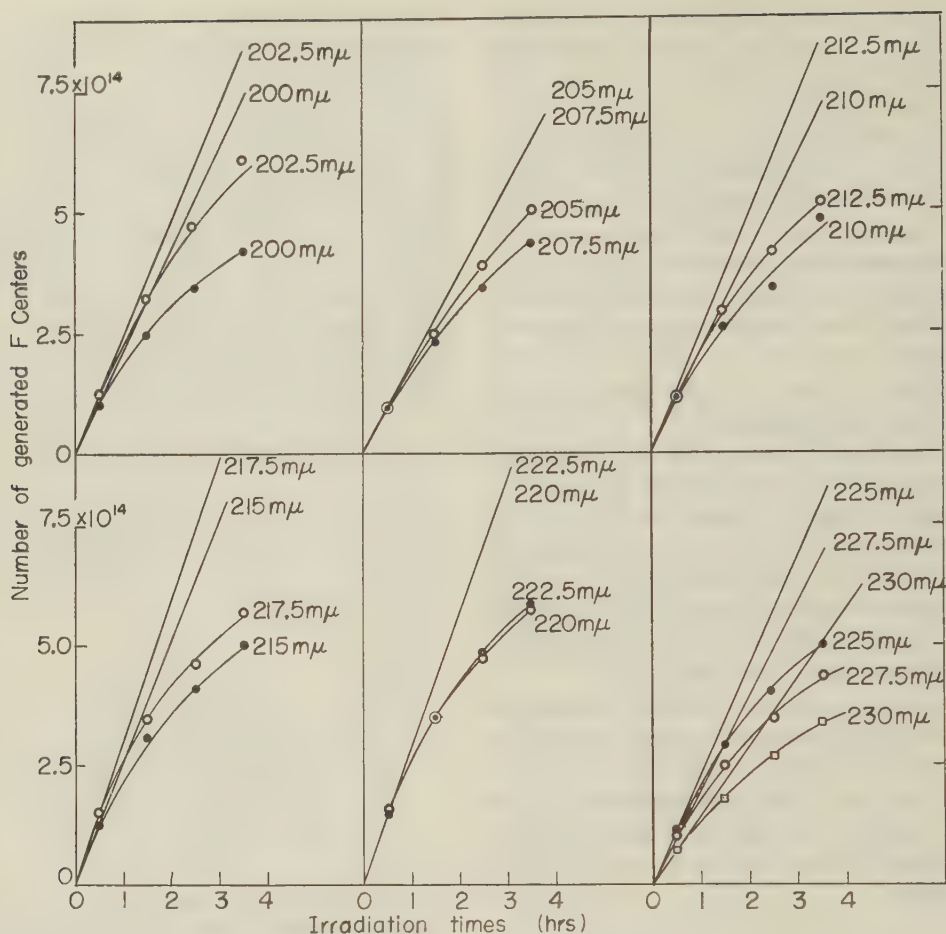


Fig. 12. Growth curves of generated F' centers versus illuminating times and slopes of these curves at zero illuminating time with several monochromatic wavelengths.

absorption curve of the crystal, which are shown in curves (b) and (c), respectively. Curve (d) is the spectral variation of η thus obtained.

In this case the yield at the wavelength of the U absorption peak (λ 228 $m\mu$) was normalized to have the same value as in the case of high concentration of U centers. From the curve (d), it is seen that the spectral variation of η between λ 232 $m\mu$ –215 $m\mu$ is the same as that in the high concentration of U centers, (cf. Fig. 3), but the maximum yield is 60 percent and its position shifts to the longer wavelength side.

For light of wavelength shorter than 200 $m\mu$, it is quite interesting to obtain a slope as shown in Fig. 12 to know the quantum yield with light which is absorbed in the fundamental absorption band, but unfortunately the number of generating F centers is

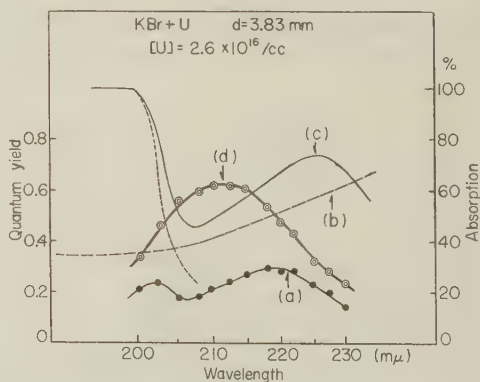


Fig. 13. Variation of quantum yield in KBr crystal containing small U center concentration.
(a) Distribution of F centers.
(b) Spectral intensity distribution of light.
(c) Absorption curve of the crystal (%).
(d) Variation of quantum yield with illuminating photon energy.

too small to be measured accurately. However, from the value at λ 200 $m\mu$ in Fig. 13 it may be said that the yield will be about 30 percent, because of the fact that here the absorption of the crystal consists mainly of the fundamental absorption tail, and the superposition of the absorption due to U centers is small.

Accepting the value of 30% by light in the exciton band, the maximum yield of 60% is explained by the following consideration.

From the result in the case of high concentration of U centers, it is observed that the quantum yield increases as the illuminating photon energy does, and it is 0.8 at 210 $m\mu$ where the absorption coefficient of the fundamental absorption tail is negligible compared to that of the U band. The yield at λ 210 $m\mu$ should be independent of the U center concentration if the light is absorbed by U centers only. However, in the case of low concentration of U centers, the absorption due to the exciton and U bands are superimposed in nearly equal amount at λ 210 $m\mu$ as shown in Fig. 13. Therefore, the yield will be reduced and have a value of 0.55 which is the mean value of 0.3 and 0.8 due to the exciton and U -light, respectively.

§ 4. Conclusion and Discussion

From the results shown in Fig. 3, it is clear that the increase of quantum yield from λ 250 $m\mu$ to 210 $m\mu$ is the property of the U band itself because the absorption due to the exciton band is negligibly small in these spectral ranges.

At a wavelength of 203 $m\mu$ the absorption of exciton and U -bands are contributing to the absorption coefficient of the crystal in equal amount and furthermore here, η is very close to unity.

From these facts it is concluded that the η 's of $U \rightarrow F$ conversion by exciton light or the light in the shorter wavelength tail of the U -band are both unity.

From the experiments of the dependence of η by the exciton band-lights upon U center concentration, it was observed that η starts to decrease when the U center concentration is below $5 \times 10^{16}/c.c.$ This fact will indicate the exciton migration through the crystal, and show that the maximum migration length is the order of one hundred lattice spacing

at room temperature: i.e. $\sim 3 \times 10^{-6}$ cm.

There might be an ambiguity that the fundamental absorption tail is affected by the existence of U centers and α or β type-absorption bands are produced and thus the observed effect will be attributed to the special localized exciton in the vicinity of a U -center. α and β absorptions correspond to the formation of special kinds of localized excitons very close to a negative ion vacancy and an F center, respectively. Seitz⁸⁾ considered that they can attract an electron and therefore the exciton is stabilized. According to his theory, U centers will not produce the localized excitons, because it has no ability of electron affinity if the model of the U -center as an H^- ion is correct, and will not influence the fundamental absorption tail. This expectation has been confirmed by comparing the absorption curves of crystals containing hydride to that of pure salts (cf. Figs. 7 and 8 in reference 5). Therefore, the observed effect of $\eta \div 1$ in the exciton absorption band is concluded to be due to the free exciton.

One more ambiguity is concerning the purity of the crystals. When the alkali halide crystals are grown in air, they sometimes contain the hydroxyl ion: OH^- and show an absorption band near the fundamental absorption tail⁹⁾. NaCl crystals take in such impurities easily but in KCl and KBr crystals the concentration of it is small. Absorption bands of OH^- are broad and their absorption maxima are 204 $m\mu$ and 215 $m\mu$ in KCl and KBr crystals, respectively. These wavelengths are far from 183 $m\mu$ and 203 $m\mu$, respectively where the maximum yield of $U \rightarrow F$ conversion takes place.

No trace of OH^- band has been confirmed in the KBr crystals which were used here, but in KCl crystals its absorption coefficient amounts to 3 cm^{-1} , which is negligibly small compared to that of U centers. Furthermore, it is reported by Etzel and Patterson⁹⁾ that the OH band is transferred to the U band in the process of additive coloration. From these facts it is hardly considered that the observed phenomena might be attributed to the OH band.

When pure alkali halide crystals are illuminated by the light in the fundamental absorption band, F centers are generated with a quantum yield of unity in the early stage of

illumination. This effect has been observed by Smakula¹⁰⁾ and is attributed to the exciton. In our experiments for the crystals containing U centers, the Smakula effect might play some part for the F center generation. It is considered that the excitons will be captured by U centers more efficiently than negative ion vacancies to produce F centers, because of the much higher concentration of the former than the latter. However, to check how much is this contribution, a slice of pure KBr crystal was illuminated in the same manner as before, but the F center formation has been observed to saturate so quickly and the saturation value was so small. Therefore, it was safely clarified that the Smakula effect can be neglected in the determination of the quantum yield of $U \rightarrow F$ conversion.

Acknowledgements

One of the authors (M.U.) wishes to thank Professor H. Pick, Professor D. L. Dexter and

Dr. W. Martienssen for helpful discussions at the International Symposium of Color Centers at Oregon State College. This work was supported by the Scientific Research Fund of the Ministry of Education.

References

- 1) R. Hilsch and R. W. Pohl: Review Article by Pohl, *Z. Phys.* **39** (1938) 36.
- 2) N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals*, (Clarendon Press, Oxford) 147.
- 3) W. Martienssen and H. Pick: *Z. Phys.* **135** (1953) 309.
- 4) F. Seitz: *Rev. Mod. Phys.* **26** (1954) 90.
- 5) M. Ueta, M. Hirai and H. Watanabe: *J. Phys. Soc. Japan* **14** (1959) 253.
- 6) R. Hilsch: *Ann. Physik* **29** (1937) 407.
- 7) F. S. Johnson, K. Watanabe and R. Tousey: *J. Opt. Soc. Amer.* **41** (1951) 702.
- 8) F. Seitz: *J. Opt. Soc. Amer.* **41** (1951) 54.
- 9) H. W. Etzel and D. A. Patterson: *Phys. Rev.* **112** (1958) 1112.
- 10) A. Smakula: *Z. Phys.* **63** (1930) 762.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, April, 1960

Multiple-Anode Proportional Counter X-Ray Diffractometer

By Jun-ichi CHIKAWA

*Department of Physics, Faculty of Science,
Kyoto University*

(Received December 4, 1959)

Argon-filled and xenon-filled three-anode proportional counters were designed so as to attain the quantum counting efficiency of about 90% for $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation, respectively. Important properties of these counters are compared with those of NaI(Tl) scintillation counter. These proportional counters have remarkable superiority over NaI(Tl) scintillation counter in monochromatization effect upon the characteristic radiation in use of a pulse-height analyzer, though their quantum counting efficiencies for the characteristic radiation are almost the same.

A stabilizer of X-ray tube output utilizing an ionization chamber with balanced filters as a monitor was also constructed. High stability was attained without accurate regulation of the tube voltage.

§ 1. Introduction

Proportional counters used with an X-ray diffractometer were constructed by Lang^{(1), (2)}, who showed that the high monochromatization effect was attained by using a propor-

tional counter and a pulse-height analyzer. Arndt and Riley^{(3), (4)} used a proportional counter, setting the pulse-height analyzer symmetrically to detect 50% of $\text{CuK}\alpha$ radiation, and attained fairly good monochromati-

zation. Parrish and Kohler⁵⁾ found that an NaI(Tl)-scintillation counter had the quantum counting efficiency of nearly 100% for all wavelengths between 0.3 and 2.5 Å. A proportional counter constructed in an ordinary way has the quantum counting efficiency of 60~70% for $\text{CuK}\alpha$ radiation, but very low quantum counting efficiency for $\text{MoK}\alpha$ radiation. For $\text{CuK}\alpha$ radiation, however, higher monochromatization effect is obtained with a proportional counter and a pulse-height analyzer. Therefore, it is desirable to design a better counter which has both the advantages of scintillation and proportional counters. This purpose will be attained with a scintillation counter so improved as to have high energy resolution, or with a proportional counter so improved as to have high quantum counting efficiency. The former is difficult in consideration of the properties of present scintillators and photomultipliers. Therefore, the latter method was preferred here. Already, Skertchly⁶⁾ has obtained increased absorption efficiency of an argon-filled proportional counter by the expedient of designing a counter tube with diagonally opposed windows, and introducing the X-ray beam at a small angle to the window. But it has a drawback that the absorption of entrance window is increased.

In X-ray diffraction work, however, high efficiency for the particular characteristic wavelength to be measured is not only desired, but it should be combined with low efficiency for other wavelengths necessarily produced by the X-ray tube. In this respect, the optimum gas absorption efficiency of a proportional counter was determined to be about 90% for both $\text{MoK}\alpha$ and $\text{CuK}\alpha$ radiations when β -filter was employed. In order to secure such a high gas absorption efficiency, the author constructed a three-anode proportional counter and eliminated the broadening of pulse-height distribution which was produced in this type of counter, and thus high counting efficiency and high monochromatization effect were attained.

Another important factor in a counter diffractometer is stability of X-ray intensity output. Accurate measurements can be carried out by keeping constant the intensity of the characteristic radiation to be measured from the X-ray tube, since the continuous

radiation is hardly detected by a scintillation or a proportional counter combined with a pulse-height analyzer. In usual apparatus, both the tube current and the tube voltage are regulated, and if they are completely regulated and also a sealed-off tube is used, good stability of the intensity of the X-ray beam will be attained. But exact regulation of the tube voltage is difficult: The use of line regulators alone is not sufficient, since the X-ray output is very sensitive to variations in the peak voltage, and most saturated-core stabilizers, while maintaining excellent regulation of r.m.s. voltage, do not keep the peak voltage constant. Therefore, accurate measurements require a stabilizer that keeps constant the intensity of the characteristic radiation from the X-ray tube, independently of the variation of the X-ray tube voltage.

This requirement will be satisfied with a stabilizer which has a monitoring system: A constant fraction of the characteristic radiation from the X-ray tube is detected with a monitoring detector and the filament current is automatically controlled so as to keep the output from a monitoring detector constant.

A detection system of monitor used in this type of stabilizers should satisfy following necessary conditions: (1) It should detect only the characteristic radiation and hardly white radiation. (2) It should have a much better stability than that required for the intensity of the characteristic radiation in the measurement of a diffracted beam. (3) In order to control rapidly the change of the characteristic radiation, it should detect the radiation at a very high counting rate and keep relative statistical fluctuations of the output small when the radiation detected with a time constant of about 0.1 sec.

In order to monochromatize the monitoring beam, a crystal monochrometer has been used^{7), 8)} but it is unstable against variation in temperature and mechanical disturbances. Therefore, the balanced filters were used here for monochromatization⁹⁾. These filters are stable against variations above mentioned, though the degree of monochromatization attained is inferior to that with a crystal monochrometer.

A counter tube is unsuitable for the measurement of a very high intensity of the

radiation because of the effective resolving time of $1\sim 10\ \mu\text{sec}$. Crystal detectors, such as $\text{CdS}^{(10)}$ and AgI , can be used for the measurement of very high intensity of the radiation, but are unsuitable for a monitor because of unstable dark current and the spectral response. Ionization chambers can be also used for the measurement of a high intensity of the radiation^{(11), (12)}, and the proper spectral response can easily be obtained by choosing the length of absorption path and the pressure of filling gas. Finally, a sealed-off ionization chamber with the balanced filters will satisfy the above conditions.

An ionization chamber was used as a monitor by Hargreaves, Prince and Wooster⁽¹³⁾, and a stabilizer using an ionization chamber as a monitor was devised by C. K. Jones⁽¹¹⁾. In these cases, however, the monochromatization of the monitoring beam was not considered. In this paper a stabilizer using an ionization chamber with the balanced filters as a monitor will be described.

§ 2. Apparatus

The detection circuit used in this work is composed of detector, amplifier, pulse-height analyzer, rate-meter and scaler in an ordinary way, as shown in Fig. 1. The stabilizer of X-ray tube output is also shown in Fig. 1. A demountable X-ray tube used here has two windows, one of which is used for diffraction, and another in opposite side for stabilizing the X-ray output. The X-ray beam from this window of the X-ray tube is divided into two beams by two slits, which are so adjusted that two beams have equal intensities respectively. These two beams are introduced

between three plates of the ionization chamber as shown in Fig. 1. The Ni and Co foils of balanced filters are respectively placed in the paths of the two beams.

The three plates of ionization chamber are mounted in a glass envelope which has a mica window to admit X-rays. The plates are supported parallel to each other with the separation of about 15 mm. The ionization chamber was filled with argon gas at the pressure of 60 cmHg, as shown in § 3. The differences in two ionization currents produced respectively between the plates combined with Ni and Co foils is obtained from the middle plate⁽¹⁴⁾ and is fed to the D. C. amplifier. The principle of stabilizing with D. C. amplifier is the same as that of stabilizing X-ray tube current^{(12), (15)}.

§ 3. Gas Absorption Efficiency

For proportional counters. The quantum counting efficiency (QCE) of a counter is equal to the product of the gas absorption efficiency and the transmission of window⁽¹⁶⁾. A 'mylar' polyester film was used for the window of the counter, in order to secure very high transmission of X-rays. So, the gas absorption efficiency of a counter should be chosen properly so as to secure the highest value of ratio I_o/I_g , where I_o is the detected intensity of the particular characteristic radiation to be measured and I_g is the total detected intensity of all other radiations necessarily produced by the X-ray tube operated at a given voltage.

When a Cu target X-ray tube is operated on full-wave rectified 60 cys 40 kVp, the spectrum from the X-ray tube was measured with a scintillation counter and a calcite analyzer crystal, and was corrected for variations of crystal reflectivity and counter sensitivity with wavelength. The subharmonic reflection of the crystal was also corrected. In this case a $20\ \mu$ Ni filter was employed and the 'mylar' film used for the window of counter was placed in front of the scintillation counter. Thus, the intensity distribution, $I(\lambda)$, which would appear just behind the window of the proportional counter when mounted on the diffractometer was obtained

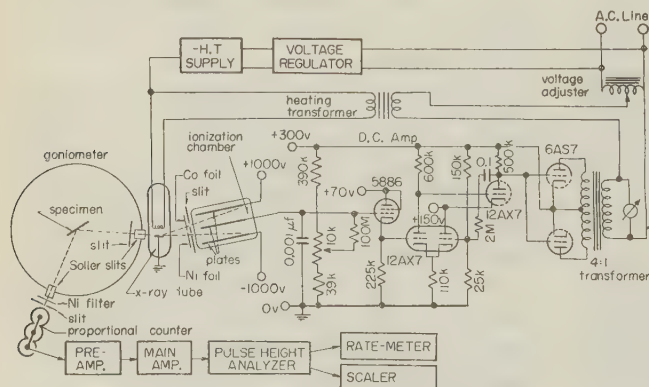


Fig. 1. The schematic diagram of apparatus and the circuit of stabilizer.

and was plotted in Fig. 2. If $Q(\lambda)$ is the gas absorption efficiency of counter tube and $D(\lambda)$ the transmission factor of a pulse-height analyzer (PHA) for a wavelength λ , then the total intensity detected with this counter is

$$\int_{\lambda_1}^{\lambda_2} I(\lambda) Q(\lambda) D(\lambda) d\lambda,$$

where λ_1 is the short wavelength limit of the spectrum and λ_2 is the effective upper limit above which absorptions of the Ni filter, the window of X-ray tube, air, etc. reduce the intensity to a negligible quantity. Consequently, we have

$$\frac{I_o}{I_g} = \frac{I_{\alpha} Q_{\alpha} D_{\alpha}}{\int_{\lambda_1}^{\lambda_2} I(\lambda) Q(\lambda) D(\lambda) d\lambda - I_{\alpha} Q_{\alpha} D_{\alpha}}$$

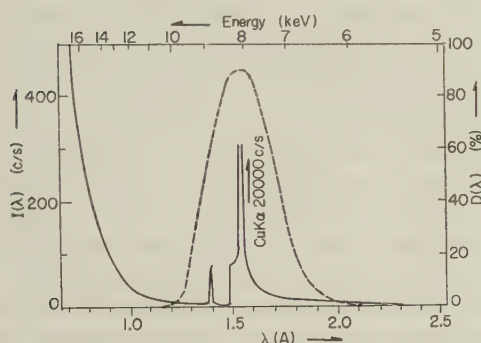


Fig. 2. Intensity distribution $I(\lambda)$ of the spectrum from a Cu target X-ray tube (40 kVp full-wave rectification) in use of 20μ Ni filter (solid line), and transmission factor $D(\lambda)$ of a pulse-height analyzer set symmetrically to detect 90% of $\text{CuK}\alpha$ with A-filled proportional counter (dotted line).

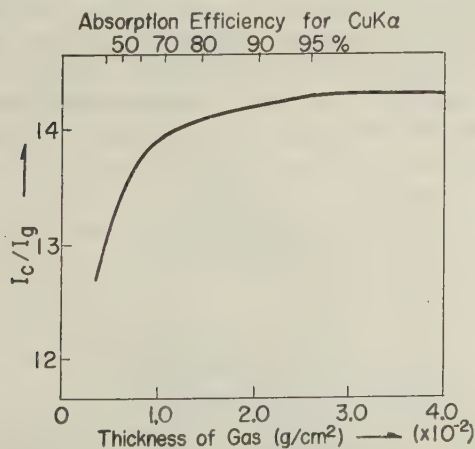


Fig. 3. The ratio of the detected intensity of $\text{CuK}\alpha$ to that of general radiation, I_o/I_g , as function of thickness of argon (g/cm^2).

where Q_{α} and D_{α} are respectively the gas absorption efficiency and the analyzer transmission for $\text{CuK}\alpha$ and I_{α} is the integrated intensity of $\text{CuK}\alpha$ radiation.

It is proper to set the window of PHA symmetrically to detect 90% of $\text{CuK}\alpha$ radiation in general case. With 90% analyzer transmission of the $\text{CuK}\alpha$ radiation, the transmission factor $D(\lambda)$ for argon-proportional counter (A-PC) was calculated from the approximation for the pulse-height distribution (PHD) explained by Lang¹⁷⁾, and was plotted in Fig. 2. The effect of the escape peak due to argon fluorescent X-ray (2.96 keV) on the PHD was not taken into account. For the $D(\lambda)$ given above, I_o/I_g was numerically calculated for various thicknesses (g/cm^2) of argon gas filled in the counter tube and was plotted in Fig. 3. The figure shows that the high value of I_o/I_g is obtained with markedly high gas absorption efficiency for $\text{CuK}\alpha$ radiation, and it is unfavorable to use A-PC with low absorption efficiency. With $D(\lambda)$ for Xe-PC obtained by Parrish and Kohler⁵⁾, in which the effect of the escape peak due to xenon fluorescent X-ray (about 4 keV) was taken into account, the estimation of I_o/I_g for Xe-PC resulted in a curve similar to that for A-PC, but the curve shows the maximum of I_o/I_g at the absorption efficiency of about 90% for $\text{CuK}\alpha$, and I_o/I_g is reduced a little with increasing the thickness of gas (g/cm^2) beyond that required for the absorption efficiency of about 90% for $\text{CuK}\alpha$. For A-PC, the maximum of I_o/I_g appears at the absorption efficiency of 93% for $\text{CuK}\alpha$, if a 17μ Ni filter is used instead of 20μ one. With a Mo target X-ray tube operated at 50 kVp and a $60 \text{ mg}/\text{cm}^2$ Zr filter, I_o/I_g was also calculated for Xe-PC in the same way, and it was found that I_o/I_g has the maximum at the absorption efficiency of 91% for $\text{MoK}\alpha$. The non-X-ray background is increased with greatly increasing absorption efficiency as will be shown later. Consequently, in use of β -filter, it is proper to choose the thickness (g/cm^2) of filling gas so as to have the absorption efficiency of about 90% for the characteristic wavelength to be measured.

For monitoring ionization chamber. The optimum gas absorption efficiency of ionization chamber used as a monitor for a Cu target X-ray tube was determined as follows:

The thickness of balanced filters must be first considered. If the ionization current i_{Ni} is produced between the plates combined with the Ni foil and i_{Co} between those combined with the Co foil, it is proper to choose the thickness of the filters such that the expected relative error for $(i_{Ni}-i_{Co})$, namely

$$\frac{(i_{Ni}+i_{Co})^{1/2}}{i_{Ni}-i_{Co}}$$

becomes a minimum¹⁸⁾. The thicknesses that satisfy this condition depend on the spectral distribution of the intensity in the incident beam and the spectral response of the ionization chamber. However, this optimum thickness has only a slight variation, notwithstanding that the spectral distribution of the intensity and the spectral response of ionization chamber vary in a wide range. (In this case, however, the expected relative error for $(i_{Ni}-i_{Co})$ has a larger variation.) The proper thickness of Ni foil is about 10 mg/cm².

In order to reduce the statistical fluctuation of output voltage of the ionization chamber, it is required to increase the intensity of incident beam as greatly as possible by broadening the width of the slits. But the upper limit of the ionization current is caused by the production of space charge. Therefore, under the condition that i_{Ni} cannot be increased beyond a given value, the gas absorption efficiency of ionization chamber should be determined such that the expected relative error for $(i_{Ni}-i_{Co})$ becomes a minimum. By a simple consideration, it is proper to choose the gas absorption efficiency in such a way that the value of i_o/i_g becomes a maximum, where i_o is the ionization current produced by the incident X-ray with the wavelengths in the window region of balanced filters and i_g in the outside of the window region.

A 10 μ mica film was used as the window of the ionization chamber. The spectral distribution of the intensity of incident beam just behind the mica window $I(\lambda)$ was obtained from the measurement with a Ni foil (10 mg/cm²) as before, after the correction for the wavelength variation of the absorption in the intervening air between the windows of the X-ray tube and the counter tube. The ionization current produced by X-ray beam with a wavelength λ is proportional to

the gas absorption efficiency $Q(\lambda)$ and inversely to λ , so that the ratio:

$$\frac{i_o}{i_g} = \frac{\int_{\lambda_{Ni}}^{\lambda_{Co}} \frac{1}{\lambda} I(\lambda) Q(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} \frac{1}{\lambda} I(\lambda) Q(\lambda) d\lambda - \int_{\lambda_{Ni}}^{\lambda_{Co}} \frac{1}{\lambda} I(\lambda) Q(\lambda) d\lambda}$$

should be made maximum by choosing a proper thickness of gas, where λ_{Ni} and λ_{Co} are NiK and CoK absorption edges, respectively. The optimum thickness of argon gas, 0.009 g/cm², was obtained by numerical calculation. Since the length of the plates of ionization chamber is 7 cm, argon gas was filled at the pressure of 60 cmHg at room temperature 20°C.

§ 4. Construction of Proportional Counters

The gas absorption efficiency required for the detection of $CuK\alpha$ radiation is secured with 0.023 g/cm² of argon and that for the detection of $MoK\alpha$ radiation with 0.059 g/cm² of xenon, from the results in § 3. In order to secure these thicknesses of gas with a side-window type counter tube designed in an ordinary way, high pressure of gas as well as large diameter of counter tube are required, so that high voltage is required to be applied to the counter tube and it will cause noise due to electric leakage. And also a thin window of counter tube will be broken by filling gas at high pressure. Although greatly increased gas absorption efficiency is easily obtained by use of end window type, the elimination of both the inactive length and the end effect upon the field, which has been suggested by Cockroft and Curran¹⁹⁾, will be difficult in practice.

Therefore, the high absorption efficiencies were secured with a combination of three

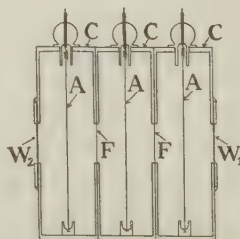


Fig. 4. Cross section of the three-anode proportional counter. A: anode wire, C: cylindrical cathode, F: polyester film, W₁: entrance window, W₂: exit window.

Table I. Three-anode proportional counters constructed here.

	counter I	counter II
radiation detected properly	CuK α	MoK α
kind of gas filled	A(90%)+CH ₄ (10%)	Xe(91%)+CH ₄ (9%)
pressure of gas filled at 20°C	132 cmHg	100 cmHg
active length	9 cm	9 cm
applied voltage	2500 V	2700 V

tubes, as shown in Fig. 4. Aluminium tubing, 10 cm long and 3 cm in diameter, was used for each unit of this counter. The anode was tungsten wire of 0.08 mm in diameter. A 'maylar' polyester film window of 0.025 mm in thickness, whose interior surface was covered with a very thin film of evaporated aluminium, was mounted in the side of the counter to admit X-rays. The exit window was an aluminium foil. A 'maylar' film of 0.006 mm thick, the both surfaces of which were also covered with a very thin film of evaporated aluminium, was mounted between the tubes in order to prevent distortion of the field. The windows in each tube have the same size of 8 mm $\times$ 20 mm. This three-anode counter was filled with argon (counter I) or xenon (counter II), as shown in Table I.

When a PC is used with an X-ray diffractometer, the sharpness of pulse-height distribution affects not only monochromatization but also reduction of non-X-ray background and escape peak. In a multiple-anode counter, broadening of the pulse-height distribution is also caused by the difference in geometry of each tube. When the three anode-wires were connected in parallel, the pulse-height distribution was as wide as that of NaI-scintillation counter. However, this disadvantage can be eliminated by adjusting voltage applied to each anode. Fig. 5 shows an adjuster of each anode voltage. The adjustment of applied voltage was as follows: A monochromatic X-ray beam was sent into the counter tube. The voltage adjuster R_1 and

R_2 in Fig. 5 was set first so as to apply +100 V to each anode wire of the first tube T_1 and the second one T_2 , while the potential of the third anode was zero. Therefore, the pulse produced in these tubes was higher than that in the third tube T_3 , so that the pulses produced in T_3 was chosen by a PHA and transmitted to a rate-meter. The window of the PHA was made narrow (about 1V) and was set on the peak of the pulse distribution. The applied voltage of tube T_2 was adjusted by R_2 in Fig. 5 so as to give the maximum counting-rate, and then that of tube T_1 was adjusted in the same way. The adjustment should be made in the order described above in consideration of statistical fluctuation.

A linear amplifier with a gain of about 21000 was used in the present experiment.

§ 5. Characteristics of the Proportional Counters

Pulse-Height Distribution. Cu target X-ray tube was operated at 30 kVp and Mo target at 50 kVp. The voltage applied to each anode of the A-filled (counter I) and the Xe-filled counter (counter II) were respectively adjusted for CuK α and MoK α characteristic radiations reflected from a calcite crystal plate.

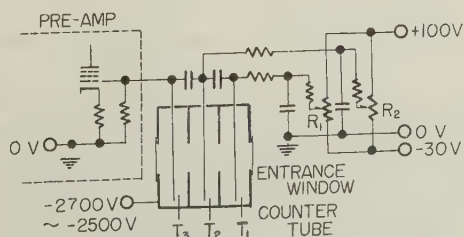


Fig. 5. Adjuster of each anode voltage.

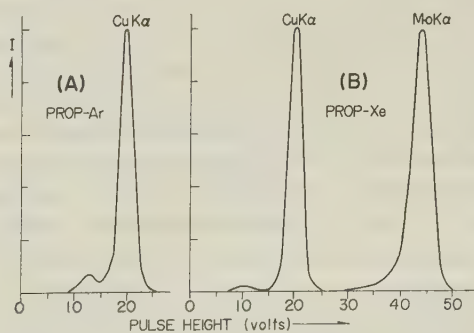


Fig. 6. Pulse-height distribution of the three-anode proportional counters. (A): A-filled, (B): Xe-filled counter.

Profiles of the pulse-height distribution curves of a single tube PC were described by Lang²⁾. In the three-anode counters, the profiles cannot be discussed exactly, because the profile depends on the exactness of adjusting the applied voltages. However, these profiles for $\text{CuK}\alpha$ are similar to those obtained by Lang^{1), 2)}, as seen in Fig. 6. The profile of the pulse-height distribution curve of the three-anode counter was also similar to that of the first tube T_1 , when the anode of T_1 only was connected with an amplifier independently of T_2 and T_3 in Fig. 5. These facts show that a noticeable broadening of the pulse-height distribution was not caused by combining three counter tubes when the voltage applied on each tube was adjusted as described in § 4.

The ratio, W/A , of the width W of the pulse-height distribution at one-half peak height to the average pulse height A is a measure of the energy resolution of the detector at a given wavelength. This ratio varies inversely as the square root of the energy of the incident X-ray quanta. For counter I, W/A for $\text{CuK}\alpha$ radiation was 16%, while W/A for continuous radiation of $\lambda = 0.77 \text{ \AA}$ (subharmonics of $\text{CuK}\alpha$) was also measured and a reasonable value of 12% was obtained. This fact shows that if the applied voltage to each tube is once adjusted for a monochromatic radiation, then for other radiations the pulse-height distribution for a three-anode counter will be also similar to that for a single tube counter.

Plateau. The plateau for the three-anode counter was similar to that for a single tube counter: The plateau of counter I for $\text{CuK}\alpha$ radiation was not more than 0.5% per 100 V in the range 2500~3000 V, while the plateau of counter II for $\text{MoK}\alpha$ radiation had almost the same value in the range 2700~3000 V. (Since the maximum voltage of the high tension power supply used here was 3000 V, the plateau above 3000 V could not be measured.) These results were obtained with an amplifier gain of about 21000 and base level of 5 V.

Non-X-ray background. The non-X-ray background was 22 c/min for counter I and 40 c/min for counter II, when the channel was used with 90% analyzer transmission for $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiations. This fact shows that the amount of this background is in-

creased by making the volume of counter tube larger and by filling gas at higher pressure. Consequently, it is unfavorable to increase volume and gas pressure of a PC beyond that required for the detection of the characteristic radiation. The background of a three-anode counter is larger than that of a SC⁵⁾, when a PHA is set. This is a drawback of a three-anode counter.

Monochromatization effect. The monochromatization effect of SC and PC with PHA will be compared here, when Cu and Mo target X-ray tubes are used. A three-anode counter with PHA is never inferior to a single anode counter constructed in an ordinary way in regard to the monochromatization effect as seen from the pulse height distribution (Fig. 6). The monochromatization effect upon $\text{CuK}\alpha$ radiation has already been reported⁵⁾, but a PC with high efficiency for $\text{MoK}\alpha$ radiation has never been constructed, so the monochromatization effect of counter II upon $\text{MoK}\alpha$ will be described in detail.

When Mo target X-ray tube was operated at 50 kVp full-wave rectification, the marked difference of PC and SC in the monochromatization effect was observed, since the

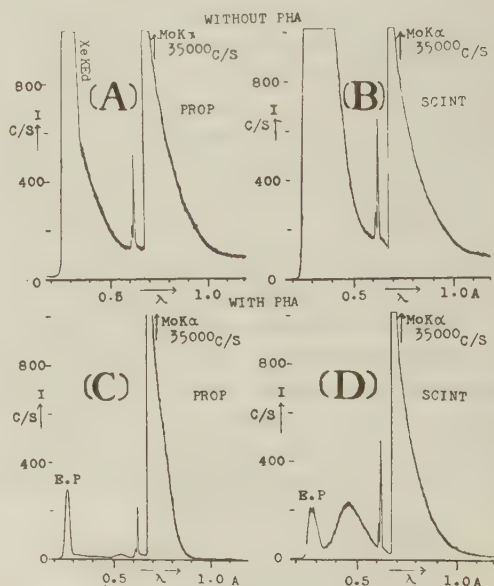


Fig. 7. Comparison of monochromatization effect of the three-anode Xe-proportional counter and the scintillation counter with pulse-height analyzer (PHA) set symmetrically to detect 90% of $\text{MoK}\alpha$, a Mo target X-ray tube operated at 50 kVp, full-wave rectification, Zr-filter (ZrO_2 80 mg/cm²) employed.

intensity of the continuous spectrum close to the $\text{MoK}\alpha$ is high. Zr filter (ZrO_2 80 mg/cm^2) was employed in all the cases described below. Fig. 7 shows the effects of both NaI-SC and counter II upon the monochromatization of $\text{MoK}\alpha$ radiation in use of PHA. Counter II and SC were compared in regard to QCE in Fig. 7(A) and (B). They show that the QCE of the PC is smaller than that of the SC for the continuous spectrum below the ZrK absorption edge, though the two counters have almost the same QCE in the longer wavelength region above $\text{MoK}\alpha$ wavelength. Marked reduction in the intensity of continuous spectrum below the ZrK absorption edge and the $\text{MoK}\beta$ radiation can be attained with the PC and PHA, owing to the high energy resolution and the low QCE for short wavelengths, as can be seen by comparing Fig. 7(C) with Fig. 7(D). The intensity of continuous spectrum above $\text{MoK}\alpha$ was also reduced with the PC and PHA, though its large portion still remained. The height of the escape peak (EP) with the SC was lower than that with the PC. This is due to the fact that the probability of escape of the fluorescent X-ray from the scintillator is smaller. However, PHA combined with PC has a narrower channel width, so that the total intensity of the escape peak with the PC is smaller.

By use of a polyethylene specimen, the backgrounds in the diffraction patterns obtained with counter II and SC are compared to each other in Fig. 8. The markedly reduced background below the position of the

(110) peak was observed with the PC in Fig. 8(A). Further, the background above the peak recorded with the PC was lower than that with the SC. NaI-SC is inferior to the PC in the monochromatization effect, as shown in Fig. 7 and 8.

Similar measurements were carried out with counter I by use of $\text{CuK}\alpha$ radiation. The peak-to-background ratio (P/B) for the polyethylene specimen was measured: The highest peak intensity with (110) line and background at $2\theta=13^\circ$ and 6° for each radiation of $\text{CuK}\alpha$ and $\text{MoK}\alpha$ were measured. I_0 is the detected intensity of the particular characteristic radiation and I_g is the total detected intensity of all other radiations necessarily produced by the X-ray tube, as have been described in §3. The spectra from X-ray tubes were measured with counters I and II and with a calcite analyzer crystal. The value of I_0/I_g at the position of the receiving slit was obtained after the corrections for variation of crystal reflectivity with wavelength and the subharmonics of the escape peak, the values obtained with the SC having been taken as unity for each radiation. The results are shown in Table II. Although the

Table II. Comparison of counters.

counter	detection efficiency, %	P/B	I_0/I_g
For $\text{CuK}\alpha$			
(40 kVp, full-wave rectification, Ni filter: 20 μ)			
A-PC (counter I)	82	92	2.5
NaI(Tl)-SC	87	32	1.0
For $\text{MoK}\alpha$			
(50 kVp, full-wave rectification, Zr filter: ZrO_2 80 mg/cm^2)			
Xe-PC (counter II)	81	58	1.9
NaI(Tl)-C	90	27	1.0

PHA set symmetrically to detect 90% of each $\text{K}\alpha$ radiation.

detection efficiency of the PC is lower a little for each $\text{K}\alpha$ radiation, the marked superiority of the PC over SC in monochromatization effect upon each $\text{K}\alpha$ radiation can be seen in Table II.

§ 6. Stability of X-Ray Tube Output

The present stabilizer was constructed for the purpose that the intensity of $\text{CuK}\alpha$ radiation from a Cu target X-ray tube was kept

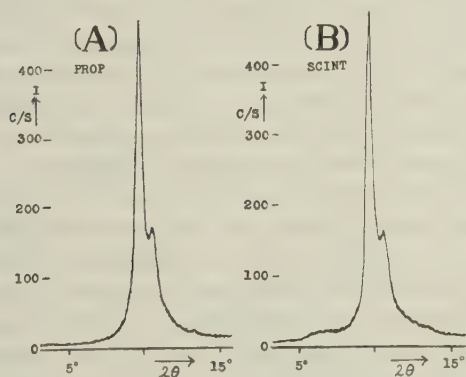


Fig. 8. Diffractometer patterns of a polyethylene obtained with the three-anode Xe-proportional counter (A) and a scintillation counter (B), to be compared in regard to intensity of the background. Mo target X-ray tube, 50 kVp, Zr-filter (ZrO_2 80 mg/cm^2).

constant independently of variation in the X-ray tube voltage. Fig. 9 shows the curve of X-ray tube voltage *versus* intensity of the (110) peak of a polyethylene specimen for X-ray tube stabilized by using the ionization chamber and the balanced filters as a monitor. The variation of X-ray tube current with tube voltage is also shown in Fig. 9. The

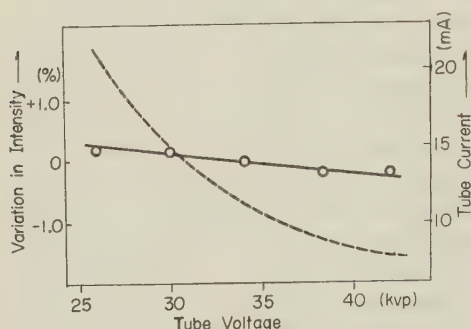


Fig. 9. X-ray tube voltage *versus* intensity of the diffracted beam and X-ray tube voltage *versus* X-ray tube current (dotted line) for a Cu target X-ray tube stabilized by using the ionization chamber and the balanced filters as a monitor.

intensities were measured by a proportional counter with a pulse-height analyzer and 20 μ Ni filter. The variation in the intensity of diffracted beam with X-ray tube voltage is not more than 0.05%/kVp, as can be seen from Fig. 9. That is, if the X-ray tube voltage is stabilized within $\pm 1\%$, the fluctuation of the intensity can be limited to $\pm 0.02\%$. (In actual case, the stability of the intensity output for long time will be limited by the stability of the D.C. amplifier used in this stabilizer.) In this apparatus the primary voltage of the high tension transformer was stabilized with an saturated-core stabilizer in order to regulate the X-ray tube voltage. To check the stability, the counter arm of the diffractometer was set at the angle of the (110) peak of the polyethylene specimen and number of counts detected in a fixed time-interval was recorded for five hours. The fluctuation of the intensity could not be observed except the statistical fluctuation.

§ 7. Discussion

Parrish and Kohler⁵⁾ reported that for MoK α the peak-to-background ratio for a silicon powder specimen was not improved by using

PC instead of NaI-SC. This may be explained by the fact that their PC had a low QCE for MoK α radiation, so that high value of I_0/I_g was not obtained, as can be seen from § 3.

The use of the higher applied voltage on Cu target X-ray tube is desirable, since it reduces the relative intensity of continuous spectrum close to the NiK absorption edge when the intensity of CuK α radiation is kept constant. For example, the increase from 40 kVp to 50 kVp in applied voltage reduces the relative intensity of the continuous radiation with $\lambda = 1.1$ Å (11 keV) to 4/5. The higher applied voltage reduces also the effective resolving time of a detector. But the intensity of the escape peak which appears in use of Xe-PC or NaI-SC (as seen in Fig. 7) is rapidly increased with the applied voltage to X-ray tube. This escape peak does not appear in A-PC. It is an advantage of A-PC over other counters that larger value of I_0/I_g is obtained with higher tube voltage.

It is convenient that a counter can be used for all diffraction work with MoK α , CuK α , FeK α , CrK α , etc. The PC was designed above for detection of CuK α only or MoK α only. However, it is not impossible to use counter II for the detection of CuK α radiation, as suggested from Fig. 3. For the detection of CuK α , only the first tube of counter II should be used with grounding other two anodes of this counter, since the detection efficiency of counter II for the continuous radiation in shorter wavelength region is large. But a small amount of the continuous radiation in shorter wavelength region remains in the spectrum of a Cu target X-ray tube obtained with the first tube of counter II, though it has the gas absorption efficiency of almost 100% for CuK α . Likewise, the two tubes (combination of T_1 and T_2 in Fig. 5) of counter I have the gas absorption efficiency of 97% for FeK α and the first tube has that of 93% for CrK α , so that good results will be obtained in diffraction work with these characteristic radiation. This is an advantage of a multiple-anode counter over a single-anode counter.

Hall, Arndt and Smith⁷⁾ described a two-window monitoring system in which X-ray beam for the diffractometer was taken from one window of the X-ray set and monitoring

beam from another. This system has not been found to be entirely satisfactory, however, owing to the fact that the monitoring beam was monochromatized by a crystal monochrometer which is unstable against variation in temperature and mechanical disturbances. If the monitoring beam is stably monochromatized and detected, good results will be obtained even in a two window monitoring system.

In the apparatus shown in Fig. 1, the wandering of the focal spot of the X-ray tube over the target will not cause variation in both the intensities of the beam irradiating a specimen and the beam introduced into the ionization chamber, because both the distance between the focal spot and the divergence slit and that between the focal spot and the slit with ionization chamber are very large compared to the wandering distance of the focal spot. But the wandering of the focal spot may cause an angular movement of the beams, which will hardly affect the intensity of beam diffracted from a powder specimen but will vary markedly the intensity of beam diffracted from a single crystal. Any monitoring system cannot eliminate such a variation in geometry as this angular movement.

Acknowledgements

The author wishes to express his sincere thanks to Prof. Kenzo Tanaka of Kyoto University for his continued guidance and encouragements throughout this work, and to Mr. M. Shiojiri for his valuable and kind assistance. This work has been carried out

by a grant-in-aid of the Ministry of Education.

References

- 1) A. R. Lang: *Nature* **168** (1951) 907.
- 2) A. R. Lang: *J. Sci. Instr.* **33** (1956) 96.
- 3) U. W. Arndt and D. P. Riley: *Proc. Phys. Soc. London A*, **65** (1952) 74.
- 4) U. W. Arndt, W. A. Coates and A. R. Craithorn: *Proc. Phys. Soc. London B*, **67** (1954) 357.
- 5) W. Parrish and T. R. Kohler: *Rev. Sci. Instr.* **27** (1956) 795.
- 6) A. H. Skertchly: *J. Sci. Instr.* **33** (1956) 209.
- 7) W. H. Hall, U. W. Arndt and R. A. Smith: *Proc. Phys. Soc. A*, **62** (1949) 681.
- 8) E. Gillam and D. G. Cole: *J. Sci. Instr.* **30** (1953) 429. E. Gillam and H. T. Heal: *Brit. J. Appl. Phys.* **3** (1952) 353.
- 9) P. A. Ross: *Phys. Rev.* **28** (1926) 425. P. A. Ross: *J. Opt. Soc. Amer. and Rev. Sci. Instr.* **16** (1928) 433.
- 10) R. Frerichs: *J. Appl. Phys.* **21** (1950) 312.
- 11) C. K. Jones: *Rev. Sci. Instr.* **24** (1953) 380.
- 12) K. Tanaka, J. Chikawa and T. Yamanaka: *J. Phys. Soc. Japan* **14** (1959) 1321.
- 13) C. M. Hargreaves, E. Prince and W. A. Wooster: *J. Sci. Instr.* **29** (1952) 82.
- 14) P. Kirkpatrick: *Rev. Sci. Instr.* **10** (1939) 186.
- 15) A. F. LeMieux and W. W. Beeman: *Rev. Sci. Instr.* **14** (1943) 130.
- 16) J. Taylor and W. Parrish: *Rev. Sci. Instr.* **26** (1955) 367.
- 17) A. R. Lang: *Proc. Phys. Soc. A*, **65** (1952) 372.
- 18) J. A. Soules, W. L. Goldon and C. H. Shaw: *Rev. Sci. Instr.* **27** (1956) 12.
- 19) A. L. Cockroft and S. C. Curran: *Rev. Sci. Instr.* **22** (1951) 37.

The Quantitative Interpretation of Luminescent Properties of Cu-Activated Calcium Orthophosphate

By Yasuo UEHARA

*Matsuda Research Laboratory, Tokyo Shibaura Electric Co. Ltd.,
Kawasaki, Japan*

(Received June 3, 1959)

In this paper, a fundamental equation of luminescence which can explain various luminescent properties of nonphotoconducting phosphors under excitation by ultraviolet of constant intensity at thermal equilibrium is formulated. According to this equation, various characteristics of Cu-activated β -calcium orthophosphate fired in a reducing atmosphere, such as temperature dependence of the quantum efficiency of fluorescence, thermoluminescence and stimulation or that of the quantum light-sum and fluorescent intensity, the build-up and fatigue of luminescence, the recovery from the fatigue of luminescence, and the relation between the fluorescent intensity and concentration of activators were calculated in detail by using an energy state model involving the ground, emitting, trapping and quenching states. Furthermore the detailed experimental results on the build-up of afterglow together with its theoretical results are described. A good agreement between the calculated and observed results was obtained.

§ 1. Introduction

The preparation and properties of Cu-activated calcium orthophosphate and related phosphors, and the qualitative interpretation of luminescent properties of Cu-activated β -calcium orthophosphate fired in a reducing atmosphere were reported in a previous paper.¹⁾ In the present paper, in addition to an explanation of the general principles of quantitative calculation of luminescent properties of nonphotoconducting phosphor, the calculated results of the various characteristics of Cu-activated β -calcium orthophosphate will be described.

§ 2. General Principles

According to the theory of adiabatic approximation concerning a system consisting of a number of nuclei and electrons, it is well known that the electronic energy states in the system are represented by the potential surfaces of multidimensions in a configuration space. Optically allowed transitions between these states are responsible for the absorption and emission of light.

Perturbation of the system represents the order of magnitude of the approximation. This perturbation is responsible for the so-called radiationless transition in the phosphor. At high temperatures, the main part of the

radiationless transition will be approximated by the absolute theory of thermal reaction,²⁾ but at low temperatures, the transition arising from the quantum mechanical resonance effect will be predominant.³⁾

The following expression for the radiationless transition probability, therefore, will be assumed as an approximation:

$$A_{ji}' = A_{ji} + k_{ji}' \quad (1)$$

with

$$k_{ji}' = \kappa_{ji} \cdot e^{-\Delta S_{ji}/k} \cdot \frac{kT}{h} \cdot e^{-\varepsilon_{ji}/kT}, \quad (2)$$

where A_{ji}' is the probability of radiationless transition due to resonance effect from state i to j and is assumed to be independent of temperature, k_{ji}' is the absolute rate constant of thermal reaction for the transition from state i to j , κ_{ji} is the transmission coefficient of electrons from state i to j , e is the base of natural logarithm, k and h are respectively Boltzmann's and Planck's constants, T is absolute temperature, ε_{ji} is the activation energy between state i and j , and ΔS_{ji} is the entropy change for the transition from state i to j , which, together with κ_{ji} , is assumed to be independent of temperature.

Let the probability of spontaneous emission for the transition from state i to j be A_{ji} and that of induced absorption be $J_{ij}B_{ji}$ in

which J_{ij} denotes the energy density of the exciting radiation, then the total probability of possible transitions from state i to j is given by

$$a_{ji} = J_{ij} \cdot B_{ji} + A_{ji} + k_{ji}' \quad (3)$$

The transition probability of induced absorption can be expressed by use of the flux density of exciting photons $n_{e,ij}$ (photons $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$) and of the absorption cross section σ_{ji} (cm^2) as follows:

$$J_{ij} \cdot B_{ji} = n_{e,ij} \cdot \sigma_{ji} \quad (4)$$

It will be possible to extend the above relations to the case of charged particle excitation by considering $n_{e,ij}$ as the flux density of secondary electrons generated by the collision of primary particles and σ_{ji} as the collision cross section for secondary electrons, neglecting the effect of the recombination process between electrons and positive holes.

The impurity activated phosphor which shows efficient luminescence is one of the typical cases in which the method of adiabatic approximation leads to a good approximation. Let us now consider a nonphotoconducting phosphor under excitation by ultraviolet radiation of constant flux density at thermal equilibrium. Let the number of activator centers per unit volume be n_0 and that of energy states in an activator center be m , the rate of change of the state density at any time t after the beginning of excitation can be given by a set of homogeneous linear differential equations, that is

$$-\frac{dn_i}{dt} = a_{ii} \cdot n_i - \sum_j' a_{ij} \cdot n_j, \quad (i=1, 2, \dots, m) \quad (5)$$

with

$$a_{ii} = \sum_j' a_{ji}, \quad (6)$$

where n_i and n_j are respectively the state density of state i and j , the negative sign on the left side expresses the decrease of the rate and $\sum_j'$ means that we are to sum over all values of j from 1 to m except $j=i$. Substituting the change of variables

$$n_i = l_i \cdot e^{-\lambda_i t} \quad (7)$$

into Eq. (5), we can obtain the secular equation

$$[A]n - \lambda n = 0, \quad (8)$$

where the matrix $[A]$ is given by

$$[A] = [\delta_{ij} \cdot a_{ij}] \quad (9)$$

with

$$\delta_{ij} = 1, \quad \text{if } j=i, \\ = -1, \quad \text{if } j \neq i, \quad (10)$$

and n is the vector of the m -th order having the explicit form of $(n_1, n_2, \dots, n_m)$. From Eq. (8), we can obtain the characteristic equation

$$D_\lambda = \begin{vmatrix} (a_{11} - \lambda) & -a_{21} & \dots & -a_{1m} \\ -a_{21} & (a_{22} - \lambda) & \dots & -a_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ -a_{m1} & -a_{m2} & \dots & (a_{mm} - \lambda) \end{vmatrix} = 0. \quad (11)$$

In general, the m roots of this equation give the rate constants of build-up or decay which belong to m states in the activator center. For the sake of convenience, let us choose the first state as the ground state. Then it follows that

$$\lambda_1 = 0. \quad (12)$$

Referring to Eq. (11), we confine ourselves, unless otherwise noted, to the case in which the rank of the determinant is $m-1$.

Now, let iD_{i-1} be the minor of the $(1, 1)$ element of the determinant D_λ when $i=1$ and also be the corresponding minor in which the $(i-1)$ -th column is replaced by $(a_{21}, a_{31}, \dots, a_{m1})$ for the values of i 's ranging from 2 to m , then the general solution of Eq. (8) is given by

$$n_i = \sum_{j=1}^m C_j \cdot iD_{i-1}(\lambda_j) \cdot e^{-\lambda_j t}, \quad (i=1, 2, \dots, m). \quad (13)$$

Here, C_j should be determined so as to satisfy the given boundary conditions. For example, let us consider the build-up of luminescence. We can define the system by the initial condition,

$$\text{at } t=0, n_1 = n_0 \text{ and all the other } n_i \text{'s are zero.} \quad (14)$$

Then we can prove that

$$C_j = \frac{n_0}{\prod_h' (\lambda_j - \lambda_h)}, \quad (15)$$

where $\prod_h'$ means the product taking on all the values of h from 1 to m except $h=j$. Substituting this result into Eq. (13), we have

$$n_i = \sum_j \frac{n_0 \cdot iD_{i-1}(\lambda_j)}{\prod_h' (\lambda_j - \lambda_h)} \cdot e^{-\lambda_j t}. \quad (16)$$

Then, the specific intensity of fluorescence

(photons. $\text{cm}^{-3} \cdot \text{sec}^{-1}$) produced by the transition from state i to j is given by

$$\frac{dI_{i,j}}{dx} = A_{ji} \cdot n_i. \quad (17)$$

Here, we must keep in mind that, in order to satisfy the postulate that the flux density of excitation must be constant, we must confine our problems to the thin layer of phosphor of thickness dx .

Referring to Eq. (16), put $t = \infty$, then by the relation given by Eq. (12), only one term remains and it follows that

$$n_{i,e} = \frac{n_0 \cdot i D_{i-1}(0)}{\Pi(-\lambda_h)}, \quad h = (2, 3, \dots, m). \quad (18)$$

This quantity corresponds to the state density of state i at steady state and it can be verified easily that it is equivalent to the result derived from Eq. (5) by putting

$$dn_i/dt = 0.$$

If the transition of induced absorption is allowed only from the ground state to higher states, Eq. (18) is reduced to the following general formula:

$$\frac{dI_{i,j}}{dx} = A_{ji} \cdot n_{i,e} = \frac{a \cdot J_{ij} \cdot B_{ji}}{b + d \cdot J_{ij} \cdot B_{ji}}, \quad (19)$$

where a , b and d are quantities independent of excitation density.

In a similar way, we can exactly calculate almost all the characteristics of luminescent properties of nonphotoconducting phosphors. As an example we shall apply this method to Cu-activated β -calcium orthophosphate phosphor fired in a reducing atmosphere.

§ 3. Energy State Model

In order to calculate the characteristics of Cu-activated β -calcium orthophosphate, a configuration model of the luminescent center is assumed as Fig. 1. In this diagram, two suffixes used before for the transition probability are abbreviated to single suffix for the sake of convenience. In order to calculate quantitatively the characteristics of luminescence, it is only necessary to know the values of the matrix element in Eq. (9) and boundary conditions. Strictly speaking, the configuration model, as shown in Fig. 1, will be almost meaningless for real phosphor except for the case in which only one mode of vibration in the crystal lattice is predomi-

nant, but it helps us to visualize the mode of the transition of electrons in the luminescent center.

As it has been already explained in a previous paper¹⁾, the model given in Fig. 1 will be satisfactory to explain, at least quantitatively, the properties of Cu-activated β -calcium orthophosphate phosphor fired in a reducing atmosphere. In this model, the six most important energy states of Cu^+ ion in the luminescent center are adopted for the sake of reduction of the numerical calculation. The number of the adopted energy states is rather small compared with that of the possible states. As the result, we have to expect that, for example, the number of components of afterglow obtained from the calculation must be reduced, at least, by more than three. Furthermore, the transition from state 5 to 4 is omitted; therefore, the number of the components of afterglow will necessarily be reduced by one. It should be noted that the radiationless transition $2 \rightarrow 4$ with the transition probability A_2' will be assumed to be caused by radiation process of

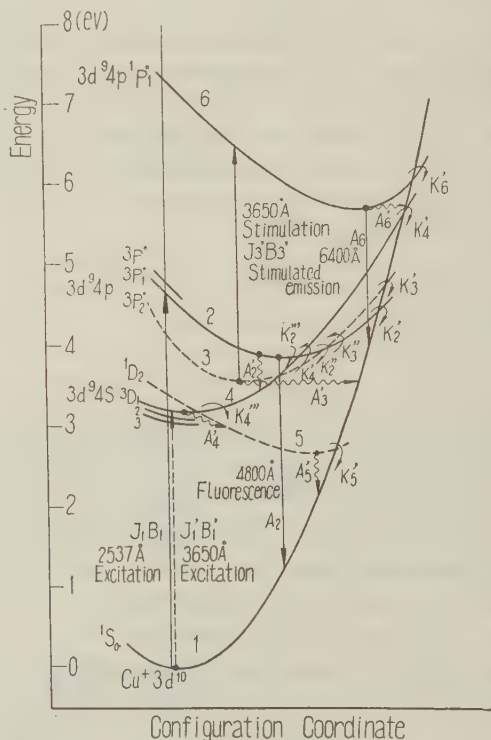


Fig. 1. Configuration coordinate model of copper-activated β -calcium orthophosphate phosphor under excitation by 2537 Å or 3650 Å.

infrared with the probability of spontaneous emission A_2' , since the transition $^3P_1^0 \rightarrow ^3D_2$ is allowed, but it will be ascribed to the radiationless transition due to dipole-quadrupole interactions between states 2 and 4. According to well known relation between the spontaneous emission probability and the frequency

of radiation, the emission probability is proportional to the third power of the frequency. Because the frequency of the infrared emission will be small, as shown in Fig. 1, the probability of spontaneous emission will be much smaller than that of radiationless transition due to $(d-q)$ interaction.

§ 4. Quantitative Calculation of Characteristics of Luminescence

(I) Quantum efficiency of fluorescence with 2537Å excitation

The fundamental equation of luminescence of the phosphor excited with 2537Å corresponding to Eq. (8) is explicitly given by

$$\begin{bmatrix} J_1 B_1 & -\pi_2' & -\pi_3' & -k_4' & -\pi_5 \\ -J_1 B_1 & \pi_2 & -k_3'' & -k_4'' & 0 \\ 0 & -k_2'' & \pi_3 & 0 & 0 \\ 0 & -\pi_2'' & 0 & \pi_4 & 0 \\ 0 & 0 & 0 & -\pi_4' & \pi_5 \end{bmatrix} n - \lambda n = 0 \quad (1.1)$$

with

$$n = (n_1, n_2, n_3, n_4, n_5),$$

where

$$\begin{aligned} \pi_2 &= A_2 + A_2' + k_2' + k_2'' + k_2''' , & \pi_2' &= A_2 + k_2' , & \pi_2'' &= A_2' + k_2''' , \\ \pi_3 &= A_3' + k_3' + k_3'' , & \pi_3' &= A_3' + k_3' , \\ \pi_4 &= A_4' + k_4' + k_4'' , & \pi_4' &= A_4' + k_4''' , \\ \pi_5 &= A_5' + k_5' , \\ J_1 B_1 &= n_{2,1} \cdot \sigma_1 . \end{aligned} \quad (1.2)$$

Here, $n_{2,1}$ and σ_1 are respectively the flux density and absorption cross section for 2537Å radiation. In Eq. (1.1), the state 6 is neglected, because it has no influence on the luminescence in this case.

According to Eq. (18), the quantum efficiency of fluorescence is given by

$$\eta_{2,f} \equiv \frac{A_2' \cdot n_{2,e}}{J_1 B_1 \cdot n_{1,e}} = \frac{1}{1 + \frac{k_2'}{A_2} + \frac{\pi_2''}{A_2} \left(1 - \frac{k_4'''}{\pi_4} \right) + \frac{k_2'''}{A_2} \left(1 - \frac{k_3'''}{\pi_3} \right)} . \quad (1.3)$$

The probability of radiationless transition A_2' , involved in the third term of the denominator in Eq. (1.3), will be of importance in connection with the quantum efficiency of fluorescence near $T=0$. If we neglect it, the quantum efficiency of fluorescence will necessarily approach to unity with decreasing temperature contrary to the result expected from experiments.

(II) Quantum efficiency of fluorescence with 3650Å excitation

The fundamental equation of fluorescence of the phosphor excited with 3650Å is given by

$$\begin{bmatrix} J_1' B_1' & -\pi_2' & -\pi_3' & -k_4' & -\pi_5 & -\pi_6 \\ 0 & \pi_2 & -k_3' & -k_4'' & 0 & 0 \\ 0 & -k_2'' & \pi_3'' & 0 & 0 & 0 \\ -J_1' B_1' & -\pi_2'' & 0 & \pi_4 & 0 & 0 \\ 0 & 0 & 0 & -\pi_4' & \pi_5 & 0 \\ 0 & 0 & -J_3' B_3' & 0 & 0 & \pi_6 \end{bmatrix} n' - \lambda n' = 0 \quad (2.1)$$

with

$$n' = (n_1', n_2', n_3', n_4', n_5', n_6'),$$

where

$$\begin{aligned} \pi_3'' &= J_3' B_3' + A_3' + k_3' + k_3'', & \pi_6 &= A_6 + A_6' + k_6', \\ J_1' B_1' &= n_{2,1}' \cdot \sigma_1' & \text{and} & & J_3' B_3' &= n_{2,3}' \cdot \sigma_3' \end{aligned} \quad (2.2)$$

with

$$n_{2,1}' = n_{2,3}'.$$

The quantum efficiency of fluorescence with 3650 Å excitation is given by

$$\begin{aligned} \eta_{2,f}' &\equiv \frac{A_2 \cdot n_{2,e}'}{J_1' B_1' \cdot n_{1,e}' + J_3' B_3' \cdot n_{3,e}'} \\ &= \frac{1}{\frac{\pi_2 \pi_4}{A_2 k_4''} - \frac{\pi_2''}{A_2} - \frac{k_2'' k_3'' \pi_4}{A_2 \pi_3'' k_4''}} \times \frac{1}{1 + \frac{\sigma_3'}{\sigma_1'} \times \frac{1}{\frac{\pi_2 \pi_3'' \pi_4}{k_2'' k_4''} - \frac{\pi_2'' \pi_3''}{k_2''} - \frac{k_3'' \pi_4}{k_4''}}}. \end{aligned} \quad (2.3)$$

As clearly seen in Eqs. (1.3) and (2.3), the quantum efficiency of fluorescence with 2537 Å excitation is independent of the excitation density, while that with 3650 Å excitation depends on the excitation density.

All values of the transition probabilities in Eqs. (1.3) and (2.3) are determined so that the calculated results for the temperature dependence of the quantum efficiency show good agreements with the observed results. A set of values selected out of many possible combinations is listed in Table I.

Table I. Numerical values of the transition probabilities estimated for Cu-activated β -calcium orthophosphate phosphor.

$$\begin{aligned} A_2 &= 1 \times 10^6 \text{ sec}^{-1}, & A_2' &= 1 \times 10^5 \text{ sec}^{-1}, & k_2' &= 5 \times 10^9 \cdot T \cdot e^{-8.7 \times 10^3/T} \text{ sec}^{-1}, & k_3'' &= 1 \times 10^4 \cdot T \cdot e^{-3 \times 10^3/T} \text{ sec}^{-1}, \\ k_3''' &= 1.5 \times 10^3 \cdot T \cdot e^{-40/T} \text{ sec}^{-1}, & A_3' &= 1 \times 10^{-5} \text{ sec}^{-1}, & k_3' &= 1 \times 10^{10} \cdot T \cdot e^{-1.8 \times 10^4/T} \text{ sec}^{-1}, \\ k_3'' &= 1 \times 10^2 \cdot T \cdot e^{-6 \times 10^3/T} \text{ sec}^{-1}, & A_4' &= 10 \text{ sec}^{-1}, & k_4' &= 1 \times 10^{10} \cdot T \cdot e^{-1.8 \times 10^4/T} \text{ sec}^{-1}, \\ k_4'' &= 1 \times 10^7 \cdot T \cdot e^{-8 \times 10^3/T} \text{ sec}^{-1}, & k_4''' &= 1 \times 10^3 \cdot T \cdot e^{-2 \times 10^3/T} \text{ sec}^{-1}, & A_5' &= 1 \text{ sec}^{-1}, \\ k_5' &= 1 \times 10^4 \cdot T \cdot e^{-3 \times 10^3/T} \text{ sec}^{-1}, & A_6 &= 1 \times 10^6 \text{ sec}^{-1}, & A_6' &= 1 \times 10^5 \text{ sec}^{-1}, & k_6' &= 7 \times 10^9 \cdot T \cdot e^{-9 \times 10^3/T} \text{ sec}^{-1}. \end{aligned}$$

In Eq. (2.3), the value of $J_1' B_1' = 1 \times 10^3 \text{ sec}^{-1}$ was assumed and the last term in the denominator was omitted, because it is negligibly small compared with unity, when the reasonable value of σ_3'/σ_1' are used. The calculated results for the temperature dependence of the quantum efficiency of fluorescence are shown, compared with the observed results, by curves (1) and (2) in Fig. 2. Their degree of agreement between the calculated and observed values seems to be rather satisfactory. Thus the model given in Fig. 1 seems to be reasonable. Although a set of numerical values of the constants listed in Table I does not seem to be necessarily the best one, we shall assume hereafter that these values are sufficiently accurate in order to investigate the detailed behaviors of the phosphor.

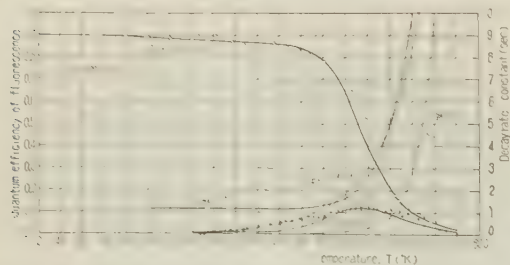


Fig. 2. Temperature dependence of the quantum efficiency of fluorescence of Cu-activated β -calcium orthophosphate under excitation by 2537 Å or 3650 Å. Full lines (Curves (1) and (2)) indicate the calculated results and points marked with $\circ$, $\times$, and $\bullet$ express the observed values. As a reference, the calculated decay rate constants of various components of afterglow are shown by curves (3), (4), and (5).

(III) Quantum efficiency of phosphorescence with 2537 Å excitation to saturation

The quantum efficiency of phosphorescence

of the phosphor excited with 2537Å to saturation is determined by the solution of Eq. (1.1) subject to the initial condition,

$$\text{at } t=0, \quad J_1=0 \quad \text{and} \quad n_i=n_{i,e}, \quad (i=1, 2, \dots, 5), \quad (3.1)$$

and it is given by

$$\eta_{2,p} = \frac{A_2 \cdot n_{2,p}}{J_1 B_1 \cdot n_{1,e}} = \eta_{2,J} [\{ 1 - (\delta_{3,p} + \delta_{4,p}) \} e^{-\lambda_{2,p} \cdot t} + \delta_{3,p} \cdot e^{-\lambda_{3,p} \cdot t} + \delta_{4,p} \cdot e^{-\lambda_{4,p} \cdot t}], \quad (3.2)$$

with

$$\begin{aligned} \delta_{3,p} &= \frac{\pi_3 \pi_4 (\pi_3 - \lambda_{3,p}) (\pi_4 - \lambda_{3,p}) + k_2'' k_3'' \pi_4 (\pi_4 - \lambda_{3,p}) + \pi_2'' \pi_3 k_4'' (\pi_3 - \lambda_{3,p})}{\pi_3 \pi_4 (\lambda_{3,p} - \lambda_{2,p}) (\lambda_{3,p} - \lambda_{4,p})}, \\ \delta_{4,p} &= \frac{\pi_3 \pi_4 (\pi_3 - \lambda_{4,p}) (\pi_4 - \lambda_{4,p}) + k_2'' k_3'' \pi_4 (\pi_4 - \lambda_{4,p}) + \pi_2'' \pi_3 k_4'' (\pi_3 - \lambda_{4,p})}{\pi_3 \pi_4 (\lambda_{4,p} - \lambda_{2,p}) (\lambda_{4,p} - \lambda_{3,p})}, \end{aligned} \quad (3.3)$$

and $n_{2,p}$ denotes the state density of state 2 at any time t after the end of excitation. Here, the rate constants of decay for the components of afterglow, $\lambda_{i,p}$ ($i=2, 3, 4, 5$), are given by the roots of the following equation:

$$F_p(\lambda) = (\pi_5 - \lambda) \{ (\pi_2 - \lambda)(\pi_3 - \lambda)(\pi_4 - \lambda) - \pi_2'' k_4'' (\pi_3 - \lambda) - k_2'' k_3'' (\pi_4 - \lambda) \} = 0. \quad (3.4)$$

Accordingly, we have

$$\lambda_{5,p} = \pi_5. \quad (3.5)$$

According to this relation, the term including $e^{-\lambda_{5,p} \cdot t}$ in Eq. (3.2) vanishes automatically, as suggested before. In general, the number of the components of afterglow is equal to that of excited states. In our case, the triplet terms of the spectrum may split completely by the interaction of crystal field, i.e. Stark effect; therefore, we can expect a number of components of afterglow.

Since the values of the roots of Eq. (3.4) can be determined by the numerical calculation, the final result reduces to

$$\eta_{2,p}(300^\circ\text{K}) = \eta_{2,J} \{ 0.99987 \cdot e^{-\lambda_{2,p} \cdot t} + 1.0288 \times 10^{-4} \cdot e^{-\lambda_{3,p} \cdot t} + 2.4577 \times 10^{-6} \cdot e^{-\lambda_{4,p} \cdot t} \} \quad (3.6)$$

with

$$\eta_{2,J} = 0.87765, \quad \lambda_{2,p} = 1.1395 \times 10^6 \text{ sec}^{-1}, \quad \lambda_{3,p} = 7.1829 \times 10^{-5} \text{ sec}^{-1}, \quad (3.7)$$

and

$$\lambda_{4,p} = 3.9180 \times 10^2 \text{ sec}^{-1} \quad \text{at } 300^\circ\text{K}.$$

The calculated values of the decay constant of the most persistent component of afterglow were 3.867 hr at 300°K, which was quite close to the observed value of 3.87 hr at 296–298°K, and 11.66 hr at 280°K. The behaviors of the calculated result given by Eq. (3.6) are rather in good agreement with the observed results reported in a previous paper¹⁾.

We can approximate $\lambda_{2,p}$, $\lambda_{3,p}$ and $\lambda_{4,p}$ to

$$\lambda_{3,p} = \pi_3 + \alpha_3, \quad \lambda_{4,p} = \pi_4 + \alpha_4 \quad \text{and} \quad \lambda_{2,p} = \pi_2 - (\alpha_3 + \alpha_4) \quad (3.8)$$

with

$$\alpha_3 = -\frac{k_2'' k_3''}{\pi_2 - \pi_3} \quad \text{and} \quad \alpha_4 = -\frac{\pi_2'' k_4''}{\pi_2 - \pi_4}, \quad (3.9)$$

if α_3 and α_4 are much smaller than π_3 and π_4 respectively, as is true in our case, then we have

$$\eta_{2,J} \cdot \lambda_{2,p} = \frac{A_2 (1 + k_2'' k_3'' / \pi_2 \pi_3 + \pi_2'' k_4'' / \pi_2 \pi_4)}{1 - k_2'' k_3'' / \pi_2 \pi_3 - \pi_2'' k_4'' / \pi_2 \pi_4} = A_2. \quad (3.10)$$

The temperature dependence of the decay constants, ($\lambda_{2,p}$, $\lambda_{4,p}$ and $\lambda_{3,p}$), which were calculated by Eqs. (3.8) and (3.9), are shown by curves (3), (4) and (5) in Fig. 2. Furthermore, it was proved directly by the numerical calculation that Eq. (3.10) holds over a wide range of temperatures from 120 to 760°K.

(IV) Quantum efficiency of phosphorescence with 3650Å excitation to saturation

The quantum efficiency of phosphorescence of the phosphor excited with 3650Å to saturation is determined by the solution of Eq. (2.1) subject to the following initial condition:

at $t=0$, $J_1'=0$, $J_3'=0$ and $n_i'=n_{i,e}'$, ($i=1, 2, \cdots, 6$). (4.1)

In a way similar to Eq. (3.2), we have

$$\eta_{2,p}' \equiv \frac{A_2 \cdot n_{2,p}'}{J_1' B_1' \cdot n_{1,e}' + J_3' B_3' \cdot n_{3,e}'}$$
$$= \eta_{2,f}' [\{ 1 - (\delta_{3,p}' + \delta_{4,p}') \} e^{-\lambda_{2,p} \cdot t} + \delta_{3,p}' \cdot e^{-\lambda_{3,p} \cdot t} + \delta_{4,p}' \cdot e^{-\lambda_{4,p} \cdot t}]$$
 (4.2)

with

$$\delta_{3,p}' = \frac{\pi_3''(\pi_3 - \lambda_{3,p})(\pi_4 - \lambda_{3,p}) + k_2'' k_3''(\pi_4 - \lambda_{3,p}) + (\pi_2 \pi_3'' - k_2'' k_3'')(\pi_3 - \lambda_{3,p})}{\pi_3''(\lambda_{3,p} - \lambda_{2,p})(\lambda_{3,p} - \lambda_{4,p})},$$
$$\delta_{4,p}' = \frac{\pi_3''(\pi_3 - \lambda_{4,p})(\pi_4 - \lambda_{4,p}) + k_2'' k_3''(\pi_4 - \lambda_{4,p}) + (\pi_2 \pi_3'' - k_2'' k_3'')(\pi_3 - \lambda_{4,p})}{\pi_3''(\lambda_{4,p} - \lambda_{2,p})(\lambda_{4,p} - \lambda_{3,p})}. \quad (4.3)$$

Since Eq. (4.3) contains the factor π_3'' , the quantum efficiency of phosphorescence in this case depends on the excitation density. The decay characteristics of afterglow under exci-

Table II. Numerical values of the coefficients in Eq. (4.2).

$J_3' B_3'$ (sec ⁻¹)	300°K				500°K			
	$\eta_{2,f}'$	$1 - (\delta_{3,p}' + \delta_{4,p}')$	$\delta_{3,p}'$	$\delta_{4,p}'$	$\eta_{2,f}'$	$1 - (\delta_{3,p}' + \delta_{4,p}')$	$\delta_{3,p}'$	$\delta_{4,p}'$
≈ 0		-3.336×10^{-4}	2.976×10^{-2}	0.9706		1.461×10^{-2}	9.948×10^{-3}	0.9754
1×10^{-2}	1.763×10^{-5}	-3.439×10^{-4}	2.122×10^{-2}	1.0001	4.704×10^{-2}	-7.578×10^{-2}	9.635×10^{-3}	0.9979
∞		-3.494×10^{-4}	1.886×10^{-11}	1.0003		-7.776×10^{-2}	3.177×10^{-7}	1.0078

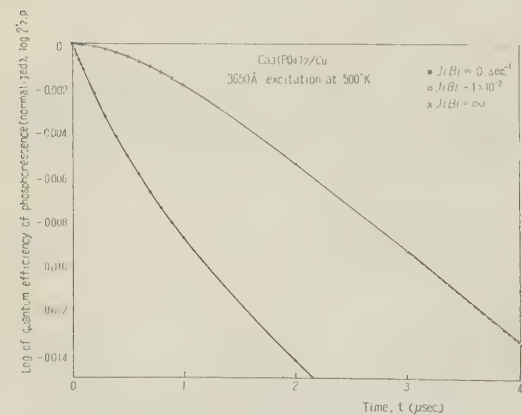


Fig. 3. Calculated decay curves of afterglow of Cu-activated β -calcium orthophosphate excited with 3650 Å of various intensities at 500°K, in microsecond time scale.

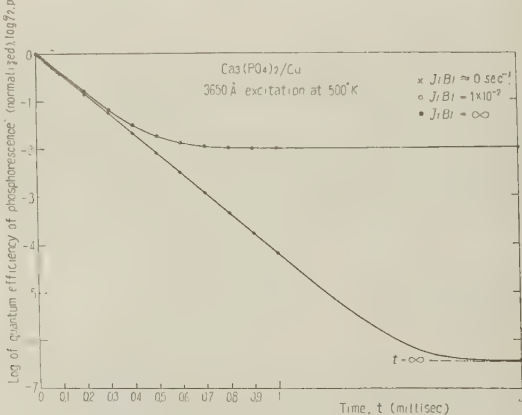


Fig. 4. Calculated decay curves of afterglow of Cu-activated β -calcium orthophosphate excited with 3650 Å of various intensities at 500°K, in millisecond time scale.

tation by 3650Å of various excitation densities at different two temperatures were calculated. The numerical values of the coefficients of three terms in Eq. (4.2), together with the quantum efficiency of fluorescence, are shown in Table II.

The calculated results for the decay characteristics of phosphorescence at 500°K are illustrated in Figs. 3 and 4. Here, we can see two significant behaviors of phosphorescence. The first is that the quantum efficiency of the persistent phosphorescence decreases rapidly with increasing excitation density. Such a property of afterglow is familiar in some other phosphors^{(4), (5)}. The second is that the coefficients of exponential functions become negative; as the result, the decay curve is given a convex curve, as shown in Fig. 3. The extremely small value of $\eta_{2,f'}$ at 300°K, as shown in Table II and Fig. 2, will be responsible for the experimental fact⁽¹⁾ that we could not observe the existence of persistent phosphorescence with 3650Å excitation at room temperature.

(V) Quantum efficiency of thermoluminescence with 2537Å excitation

Let us suppose that a thin layer of the phosphor is excited by 2537Å at $T_0^\circ\text{K}$, then, it is placed in the dark for t_0 sec which is sufficiently long to exhaust all the electrons in the excited states except for the trapping state 3, and then it is heated up to any higher temperatures $T^\circ\text{K}$ and the whole system reaches instantly thermal equilibrium at $T^\circ\text{K}$. Then the state density of state 2 at any time t after the beginning of heating is determined by the solution of Eq. (1.1) subject to the initial condition.

$$\text{at } t=0, J_1=0, n_3=n_3^0 \text{ and all the other } n\text{'s are zero.} \quad (5.1)$$

In this solution, the value of n_3^0 is determined by the calculation similar to that of Eq. (3.2) and it follows that

$$n_3^0(280^\circ\text{K}, t_0) = n_{3,e}(280^\circ\text{K}) \{ (1 - 2.0912 \times 10^{-11}) \cdot e^{-2.3881 \times 10^{-5} \cdot t_0} \\ + 2.0969 \times 10^{-11} \cdot e^{-1.1365 \times 10^6 t_0} + 5.6949 \times 10^{-14} \cdot e^{-2.3139 \times 10^2 \cdot t_0} \}. \quad (5.2)$$

Thus, with a high degree of exactness over a wide range of temperature T_0 , we have

$$n_3^0(T_0, t_0) = (n_{3,e} \cdot e^{-\lambda_{3,p} \cdot t_0})_{T_0}. \quad (5.3)$$

Using this relation, we have for the quantum efficiency of thermoluminescence

$$\eta_{2,t}(T_0, t_0, T, t) = \eta_{2,f}(T_0) \left(\frac{k_2''}{\pi_3} \cdot e^{-\lambda_{3,p} \cdot t_0} \right)_{T_0} \cdot \frac{k_3''}{(\lambda_{2,p} - \lambda_{3,p})(\lambda_{2,p} - \lambda_{4,p})} \\ \times \left\{ e^{-\lambda_{3,p} \cdot t} - \frac{(\pi_4 - \lambda_{2,p})(\lambda_{3,p} - \lambda_{4,p})}{(\pi_4 - \lambda_{3,p})(\lambda_{2,p} - \lambda_{4,p})} \cdot e^{-\lambda_{2,p} \cdot t} - \frac{(\pi_4 - \lambda_{4,p})(\lambda_{2,p} - \lambda_{3,p})}{(\pi_4 - \lambda_{3,p})(\lambda_{2,p} - \lambda_{4,p})} \cdot e^{-\lambda_{4,p} \cdot t} \right\}. \quad (5.4)$$

As an example, let $T_0=280^\circ\text{K}$, $t_0=1$ sec., $T=600^\circ\text{K}$, then we have

$$\eta_{2,t}(280^\circ\text{K}, 1 \text{ sec}; 600^\circ\text{K}, t \text{ sec}) \\ = 2.4081 \{ e^{-3.3462t} - 0.97852 \cdot e^{-2.7384 \times 10^6 \cdot t} - 0.02148 \cdot e^{-3.0471 \times 10^4 \cdot t} \}. \quad (5.5)$$

In a similar way, the quantum efficiency of thermoluminescence as a function of time t at various temperatures T adopted as a parameter was calculated and the results are shown in Figs. 5(a), the last points connected with dotted lines show the maximum values of the quantum efficiency of thermoluminescence at given temperature T . We can see that the higher the temperatures, the faster the rise time of the quantum efficiency becomes. The experimental fact⁽¹⁾ that the rise time of thermoluminescence is very fast compared with the decay time is satisfactorily explained by this calculation. The calculated decay constant for the most persistent component of thermoluminescence is $\tau_{3,t}=10.00$ sec at 460°K and it is quite close to the observed value of about 10 sec at 465°K⁽¹⁾.

The maximum values of the quantum efficiency of thermoluminescence calculated for the phosphor excited with 2537Å at temperatures $T_0=280^\circ\text{K}$ and stored in the dark for 1 sec are shown as a function of heating temperature T by curve (1) in Fig. 6, and also those cal-

culated for the phosphor excited with 2537Å and stored in the dark for 1 sec at $T_0^{\circ}\text{K}$, and then heated at temperature $T=600^{\circ}\text{K}$ are shown as a function of temperature T_0 by curve (2) in Fig. 6. These calculated results can explain satisfactorily the experimental results reported in a previous paper¹⁾.

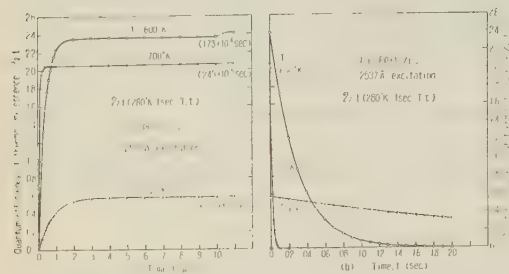


Fig. 5. Calculated build-up and decay characteristics of thermoluminescence of Cu-activated β -calcium orthophosphate phosphor excited with 2537 Å and stored in the dark for 1 sec at 280°K, and then heated at 500°, 600° and 700°K. (a) Build-up characteristics, (b) build-up and decay characteristics.

(VI) Quantum efficiency of thermoluminescence with 3650 Å excitation

By the method similar to earlier treatments, we can calculate the quantum efficiency of thermoluminescence of the phosphor excited with 3650 Å. The calculated maximum quantum efficiency of thermoluminescence is given by

$$\eta_{2,t}(280^{\circ}\text{K}, 1 \text{ sec}; 600^{\circ}\text{K}, \text{max})=4 \times 10^{-54} .$$

(6.1)

Thus the experimental fact that no thermoluminescence could be observed with 3650 Å is satisfactorily explained.

(VII) Quantum efficiency of stimulation

The quantum efficiency of stimulation for the phosphor which was first excited with 2537 Å to saturation and stored in the dark for t_0 sec, and then stimulated with 3650 Å is given by the solution of Eq. (2.1) subject to the initial condition,

at $t=0$, $n_3=n_3^0$ and all the other n 's are zero.

(7.1)

According to the earlier calculated results for the phosphorescence and thermoluminescence of the phosphor excited with 3650 Å, we can, in an approximate calculation, neglect $J_1'B_1'$ and k_4'' involved in the general solution and we have for the state density of state 6

$$n_{6,s}=\frac{n_3^0 \cdot J_3' B_3'}{(\pi_6-\lambda_3)} \left\{ \frac{(\pi_2''-\lambda_3)(\pi_6-\lambda_3)}{(\lambda_2-\lambda_3)(\pi_6-\lambda_2)} \cdot e^{-\lambda_2 \cdot t} + \frac{(\lambda_2-\pi_3'')}{(\lambda_2-\lambda_3)} \cdot e^{-\lambda_3 \cdot t} - \frac{(\pi_6+\pi_3''-\lambda_2-\lambda_3)}{(\pi_6-\lambda_2)} \cdot e^{-\lambda_6 \cdot t} \right\}$$
$$\doteq \frac{n_3^0 \cdot J_3' B_3'}{(\pi_6-\pi_3'')} \cdot (e^{-\lambda_3 \cdot t} - e^{\lambda_6 \cdot t}) ,$$

(7.2)

where λ_i denotes the rate constants of stimulation.

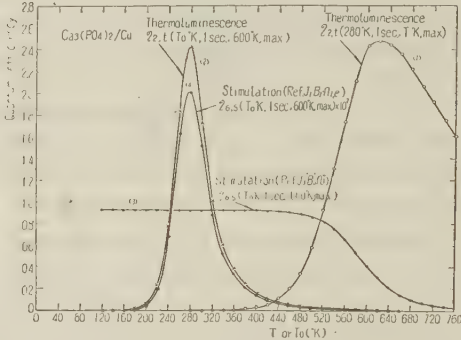


Fig. 6. Calculated temperature dependence of the quantum efficiency of thermoluminescence and stimulation of Cu-activated β -calcium orthophosphate.

Curve (1): The maximum quantum efficiency of thermoluminescence as a function of heating temperature T for the phosphor which was excited with 2537 Å, stored in the dark for 1 sec at 280°K, and then heated up to $T^{\circ}\text{K}$.

Curve (2): The maximum quantum efficiency of thermoluminescence as a function of temperature T_0 for the phosphor which was excited with 2537 Å, stored in the dark for 1 sec at variable temperature $T_0^{\circ}\text{K}$, and then heated up to 600°K.

Curve (3): Temperature dependence of the maximum quantum efficiency of stimulation which was determined with reference to the absorption of 3650 Å radiation.

Curve (4): Temperature dependence of the maximum quantum efficiency of stimulation which was determined with reference to the absorption of 2537 Å radiation.

It should be noticed that the value of curve (4) is 10^3 times enlarged.

Now, let us define the quantum efficiency of two types as follows:

$$\eta_{6,s}(t_0; J_3' B_3' \cdot n_{3,0}) = \frac{A_6 \cdot n_{6,s}}{J_3' B_3' \cdot n_{3,0}} = \frac{A_6}{(\pi_6 - \pi_3'')} (e^{-\lambda_3 \cdot t} - e^{-\lambda_6 \cdot t}), \quad (7.3)$$

$$\eta_{6,s}(t_0; J_1 B_1 \cdot n_{1,e}) = \frac{A_6 \cdot n_{6,s}}{J_1 B_1 \cdot n_{1,e}} = \frac{A_6 k_2'' \cdot J_3' B_3'}{(\pi_6 - \pi_3'')(\pi_2 \pi_3 - k_2'' k_3'')} \cdot e^{-\lambda_3 \cdot t} (e^{-\lambda_3 \cdot t_0} - e^{-\lambda_6 \cdot t}). \quad (7.4)$$

The former denotes the quantum efficiency with reference to the absorbed quanta of 3650 Å stimulating radiation and the latter that with 2537 Å exciting radiation. Taking account of the approximation given by Eq. (5.3), in Eq. (7.3), $n_{3,0}$ was used instead of $n_{3,e}$. As an example, using the values of $J_1' B_1' = J_3' B_3' = 1 \times 10^{-2} \text{ sec}^{-1}$, $t_0 = 1 \text{ sec}$ and $T = 280^\circ \text{K}$, build-up and decay characteristics of stimulation were calculated by Eq. (7.4). The calculated results are shown in Fig. 7 and are in good agreement with the observed results¹⁾.

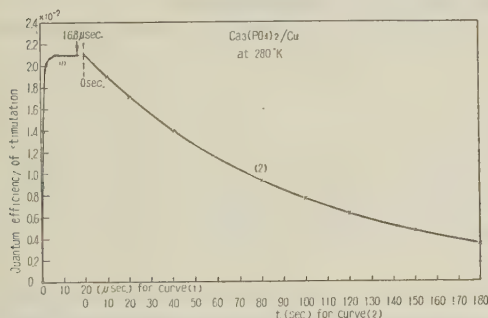


Fig. 7. Calculated build-up and decay characteristics of stimulation of Cu-activated β -calcium orthophosphate which was excited with 2537 Å to saturation, stored in the dark for 1 sec, and then irradiated with 3650 Å at 280°K.

The temperature dependence of the maximum quantum efficiency of stimulation, which was calculated by Eqs. (7.3) and (7.4) using the same values for $J_1' B_1'$, $J_3' B_3'$ and t_0 as given above, is shown by curves (3) and (4) in Fig. 6, respectively. The calculated curves (2) and (4) are sufficiently satisfactory to explain quantitatively the experimental fact that the brightest thermoluminescence and stimulated red emission were observed with 2537 Å excitation at about 280°K, as reported in a previous paper¹⁾. The small value of the quantum efficiency of stimulation, as given by curve (4) in Fig. 6, can explain the observed weak intensity of the stimulated red emission.

(VIII) Quantum light-sum of luminescence with 2537 Å excitation

Now let us define the quantum light-sum of luminescence by the integral of the quantum efficiency over the entire time interval of the emission. The quantum light-sum of phosphorescence, thermoluminescence and stimulation calculated by using Eqs. (3.2), (5.4) and (7.4) under the same conditions given before are shown by curves (1), (2) and (3) in Fig. 8, respectively. It is of interest that the quantum light-sum of thermoluminescence is larger than that of phosphorescence over the wide range of temperatures, while that of stimulation is larger than that of phosphorescence in the limited range of temperatures. These results are quite reasonable compared with the observed results in sulfide phosphors reported by Ellickson⁶⁾.

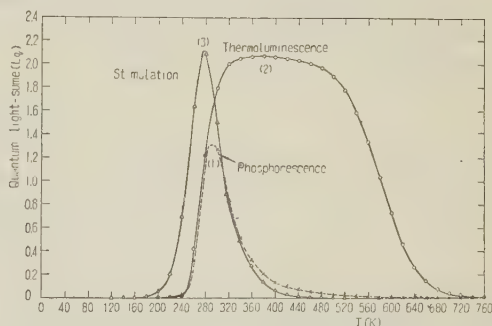


Fig. 8. Calculated temperature dependence of the quantum light-sum of phosphorescence, thermoluminescence and stimulation of Cu-activated β -calcium orthophosphate.

Curve (1): Temperature dependence of the quantum light-sum of phosphorescence of the phosphor excited with 2537 Å to saturation.

Curve (2): Temperature dependence of the quantum light-sum of thermoluminescence of the phosphor which was excited with 2537 Å to saturation, stored in the dark for 1 sec at 280°K, and then heated up to $T^\circ \text{K}$.

Curve (3): Temperature dependence of the quantum light-sum of stimulation of the phosphor which was excited with 2537 Å to saturation, stored in the dark for 1 sec, and then irradiated with 3650 Å.

(IX) *Build-up and fatigue of luminescence with 2537Å excitation*

According to Eq. (16), the general solution for build-up of luminescence of the phosphor excited with 2537Å for t_b sec is given by

$$n_{1,b} = n_0 \left[\frac{\pi_5(\pi_2\pi_3\pi_4 - \pi_2''\pi_3k_4'' - k_2''k_3''\pi_4)}{\lambda_{2,b} \cdot \lambda_{3,b} \cdot \lambda_{4,b} \cdot \lambda_{5,b}} + \sum_{j=2}^5 \frac{(\pi_5 - \lambda_{j,b}) \{ (\pi_2 - \lambda_{j,b}) (\pi_3 - \lambda_{j,b}) (\pi_4 - \lambda_{j,b}) - \pi_2'' (\pi_3 - \lambda_{j,b}) k_4'' - k_2'' k_3'' (\pi_4 - \lambda_{j,b}) \}}{\prod_h' (\lambda_{j,b} - \lambda_{h,b})} \cdot e^{-\lambda_{j,b} \cdot t_b} \right], \quad (9.1a)$$

$$n_{2,b} = J_1 B_1 n_0 \left\{ \frac{\pi_3 \pi_4 \pi_5}{\lambda_{2,b} \cdot \lambda_{3,b} \cdot \lambda_{4,b} \cdot \lambda_{5,b}} + \sum_{j=2}^5 \frac{(\pi_3 - \lambda_{j,b}) (\pi_4 - \lambda_{j,b}) (\pi_5 - \lambda_{j,b})}{\prod_h' (\lambda_{j,b} - \lambda_{h,b})} \cdot e^{-\lambda_{j,b} \cdot t_b} \right\}, \quad (9.1b)$$

and so on, where $\lambda_{j,b}$ denotes the rate constant of build-up of luminescence.

The specific intensity and quantum efficiency of build-up of luminescence are respectively given by

$$\frac{dI_{2,b}}{dx} = A_2 \cdot n_{2,b} \quad (9.2)$$

and

$$\eta_{2,b} = \frac{A_2 \cdot n_{2,b}}{J_1 B_1 \cdot n_{1,b}}. \quad (9.3)$$

Substituting Eq. (9.1) into Eqs. (9.2) and (9.3), and using the numerical values given in Table I and those of $\lambda_{j,b}$, the characteristics of build-up of luminescence for various values of the parameter $J_1 B_1$ were calculated. The calculated results are illustrated in Figs. 9, 10, 11 and 12. In Figs. 9 and 10, the specific intensity of luminescence at steady state is

always normalized to unity, while in Fig. 12, the maximum of the specific intensity of luminescence is normalized to unity.

The characteristics of build-up of luminescence are not, in general, given by a simple curve, but show a certain number of maxima or minima. The number of maximum or minimum points decreases with decreasing

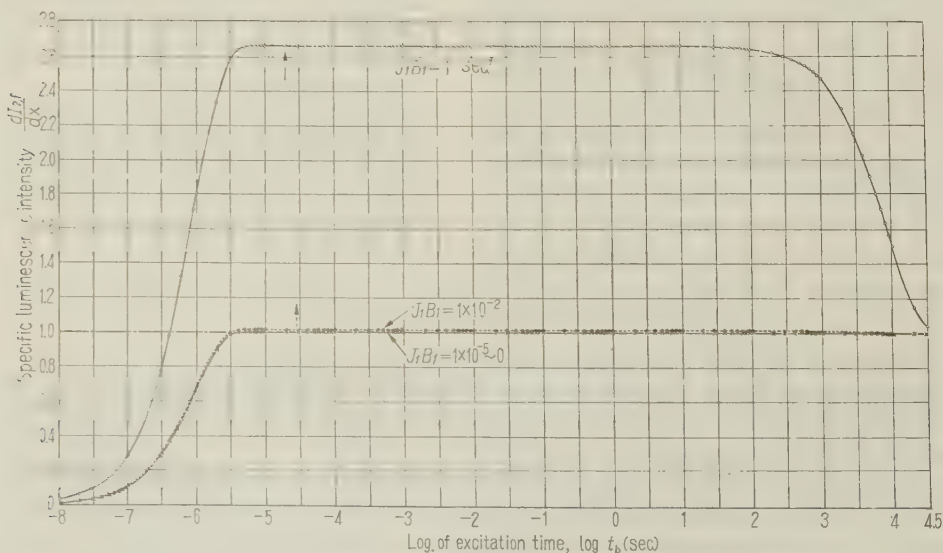


Fig. 9. Calculated characteristic curves of build-up of Cu-activated β -calcium orthophosphate excited with 2537Å of various intensities corresponding to $J_1 B_1 = 1 \sim 0 \text{ sec}^{-1}$ at 300°K. Arrows show the position of maximum points.

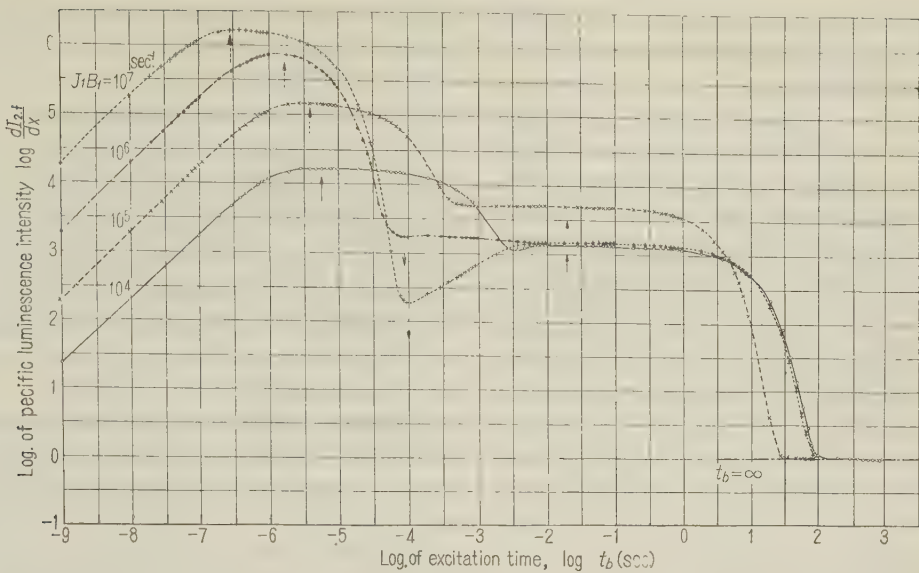


Fig. 10. Calculated characteristic curves of build-up of Cu-activated β -calcium orthophosphate excited with 2537 Å of various intensities corresponding to $J_1 B_1 = 10^4 \sim 10^7 \text{ sec}^{-1}$ at 300°K. Arrows show the position of the maximum or minimum points.

excitation density and finally the build-up curve monotonously approaches to the saturation value of luminescence. The shape of

the build-up curves shown in Fig. 10 is quite different from that of the curves which have already been reported^{4),7)}, but it rather resembles that of the curves obtained by Gessner⁸⁾ in zinc sulfide phosphor under excitation by nuclear radiation, disregarding the difference of units in the time scale. Such a result as shown in Fig. 10 is important when the phosphor is used as a scintillator and is proved to be reasonable for the explanation of the characteristics of scintillator, which will be reported elsewhere.

The curve shown in Fig. 12, which was reproduced from the curve of $J_1 B_1 = 1 \text{ sec}^{-1}$ in Fig. 9 by plotting it in a linear scale instead of semilog scale, is considered as a typical case expressing the characteristics of the fatigue of luminescence such as already observed by some workers⁹⁾ in various phosphors. Accordingly, we can interpret the fatigue of luminescence as a process of the saturation of luminescence in the course of the build-up of luminescence.

(X) Recovery from the fatigue of luminescence

Let us now consider the recovery from the fatigue of luminescence for the phosphor which was first excited by 2537 Å to saturation and then placed in the dark for a long time after the end of excitation. Let us ex-

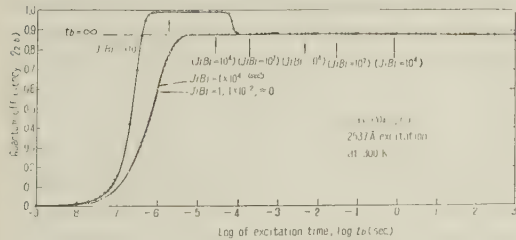


Fig. 11. Calculated quantum efficiency of Cu-activated β -calcium orthophosphate excited with 2537 Å of various intensities at 300°K as a function of excitation time.

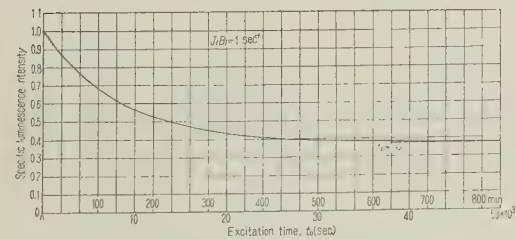


Fig. 12. Calculated relation between the specific intensity and excitation time for Cu-activated β -calcium orthophosphate excited with 2537 Å of an intensity corresponding to $J_1 B_1 = 1 \text{ sec}^{-1}$ at 300°K. This curve was reproduced from the corresponding curve in Fig. 9 by plotting it in a linear scale instead of semilog scale.

press the rate of recovery from the fatigue of luminescence at any time t after the end of excitation by

$$\theta_R = \frac{n_{1,r} - n_{1,e}}{n_0 - n_{1,e}}, \tag{10.1}$$

where $n_{1,r}$ denotes the state density of the ground state at time t .

The fatigue of luminescence and its recovery depend on the excitation density and temperature. As an example, therefore, the characteristics of the recovery from the fatigue of luminescence under excitation by 2537Å of an excitation density given by J_1B_1

=1 sec⁻¹ at 300°K was calculated. The calculated result is given be

$$\begin{aligned} \theta_R = 1 - & \{ 4.383 \times 10^{-7} \cdot e^{-\lambda_2 \cdot p \cdot t} \\ & + 1.0096 \cdot e^{-\lambda_3 \cdot p \cdot t} - 1.011 \cdot e^{-\lambda_4 \cdot p \cdot t} \\ & + 5.356 \times 10^{-4} \cdot e^{-\lambda_5 \cdot p \cdot t} \} . \end{aligned} \tag{10.2}$$

This result is illustrated in Fig. 13 and seems to be reasonable compared with the observed results for the other some phosphors which was reported by Beese and Marden⁹⁾.

(XI) Build-up and saturation of afterglow with 2537Å excitation

(a) Theoretical

The state density of various states in the phosphor excited with 2537Å of constant intensity for t_b sec has already been calculated and given by $n_{i,b}$ ($i=1, 2, \dots, 5$) in Eq. (9.1). Using these values, the build-up of afterglow under excitation by 2537Å of constant intensity can be determined by the solution of Eq. (1.1) subject to the initial condition.

$$\begin{aligned} \text{at } t=0, J_1=0 \text{ and } n_i &= n_{i,b} \\ (i=1, 2, \dots, 5) \end{aligned} \tag{11.1}$$

In a way similar to Eq. (3.2), the state density of state 2 at any time t after the end of excitation was determined, and then the specific intensity of all the components of

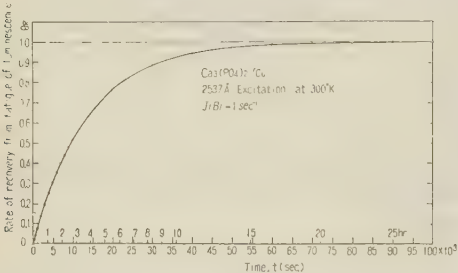


Fig. 13. Calculated curve of the rate of recovery from the fatigue of luminescence for Cu-activated β -calcium orthophosphate excited to saturation by 2537 Å of an excitation density given by $J_1B_1=1 \text{ sec}^{-1}$ at 300°K.

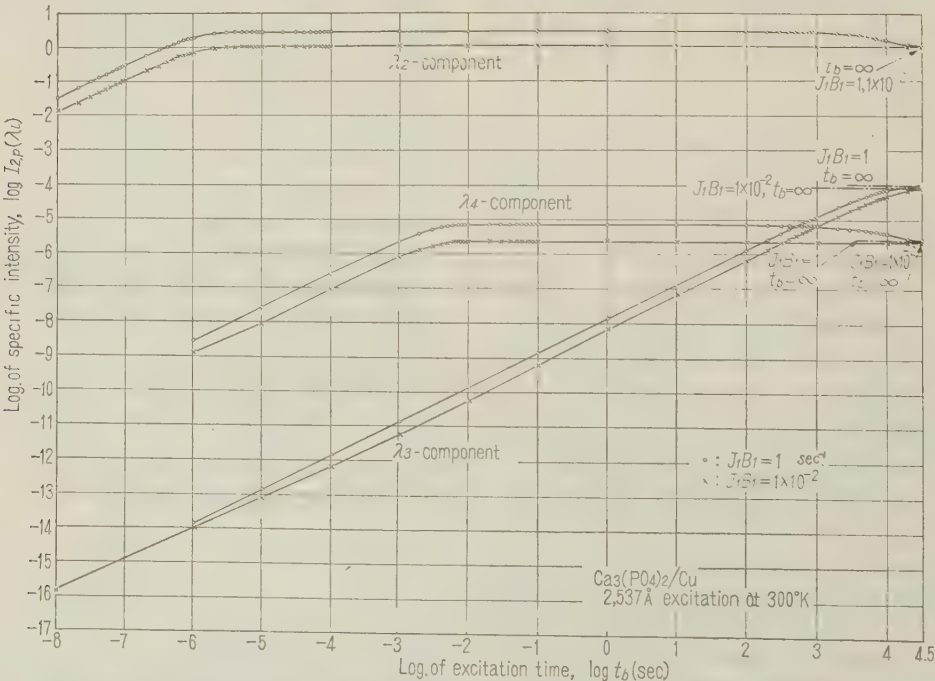


Fig. 14. Calculated curves of build-up of the specific intensity of various components of afterglow of Cu-activated β -calcium orthophosphate under excitation by 2537 Å at 300°K.

afterglow was calculated. As an example, the calculated characteristic curves of the afterglow at $t=0$ for two different excitation densities are shown in Fig. 14. As clearly seen in this diagram, the specific intensity of all the components of afterglow increases rapidly with increasing excitation time t_b and then gradually approaches to its maximum or saturation value. All these curves reach the values near maximum or saturation at excitation time corresponding to their decay constants of afterglow. As the result, the smaller the decay constant, the shorter the excitation time required for reaching the maximum or saturation of afterglow.

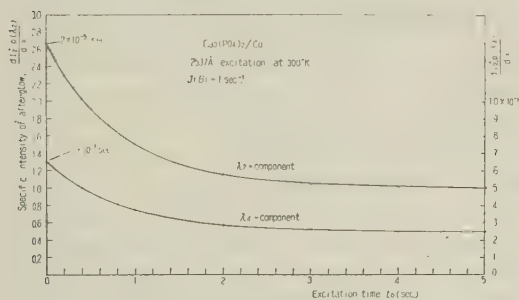


Fig. 15. Calculated build-up curves of λ_2 - and λ_4 -component of afterglow of Cu-activated β -calcium orthophosphate reproduced from the λ_2 - and λ_4 -curve in Fig. 14 by plotting in linear scale instead of log-log scale.

The specific intensity of the most persistent component of afterglow, i.e. λ_3 -component, approaches monotonously to its saturation value with increasing excitation time, as shown in Fig. 14, while that of λ_2 - or λ_4 -component of afterglow reaches its saturation value through a maximum point, as shown in Fig. 15 which is plotted in linear scale. It seems that λ_2 - and λ_4 -curve express the typical characteristics of negative pre-excitation effect of phosphorescence and characteristics of λ_3 -curve correspond to positive pre-excitation effect⁽¹⁰⁾. If the phosphor shows an appreciable photochemical deterioration, even the most persistent component of phosphorescence will exhibit negative pre-excitation effect as will be reported elsewhere.

(b) Experimental

In order to check the theoretical results mentioned above by experiments, the characteristics of build-up of phosphorescence for the phosphor under excitation by strong

2537Å were measured accurately. A thin layer of the phosphor, which was stored in the dark for more than 24 hr in order to exhaust the phosphorescence completely, was excited with 2537Å radiation of constant intensity from a 20 watt low pressure mercury discharge lamp made with quartz. The phosphor layer was placed at a constant distance of about 2 cm from the mercury lamp. A series of excitation times of 10 sec, 30 sec, 2 min, 10 min, 1 hr, 3 hr and 6 hr were used. The decay curves of phosphorescence were automatically recorded with a Brown Elektronik Recording Electrometer combined with a photomultiplier during the period from about 1 to 100 min after the end of excitation. All these experiments were carried out at 297–298°K. As an example, the observed values of decay characteristics of phosphorescence for the phosphor excited for 3 hr are shown in Fig. 16. In this diagram, the observed values were adopted from the original continuous decay curve at a period of 0.5–2 min.

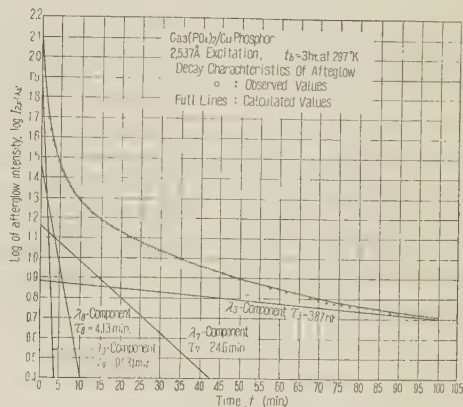


Fig. 16. Observed decay characteristics of afterglow of Cu-activated β -calcium orthophosphate under strong excitation by 2537 Å for 3 hours at 297°K. Full lines indicate the decay characteristics of afterglow calculated by analyzing the observed result.

The observed decay curve was resolved into four components of phosphorescence having the decay constants of $\tau_3 = 3.87 \text{ hr}$, $\tau_7 = 24.6 \text{ min}$, $\tau_8 = 4.13 \text{ min}$ and $\tau_9 = 0.931 \text{ min}$ shown by the four straight lines in this diagram which was plotted in semilog scale. The resultant curve is shown by the full line and shows a good agreement with observed value. Thus the intensity of the four components of phosphorescence at $t=0$, $I_{2,p}(\lambda_i)$ ($i=3, 7, 8, 9$),

were determined accurately. By the same way, those for all the other excitation times were determined. The initial intensity of the four components of phosphorescence as a function of excitation time is shown in Fig. 17. As seen in this diagram, at least, λ_3 - and λ_8 - component show clearly the characteristics corresponding to positive and negative pre-excitation effect, respectively. Although it is not clear, the behaviors of λ_7 - and λ_8 - component seem to be negative effect.

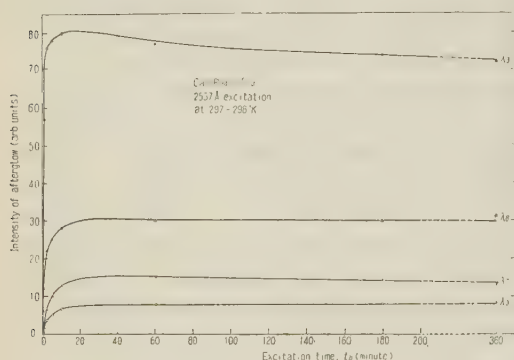


Fig. 17. Observed build-up curves of the components of afterglow of Cu-activated β -calcium orthophosphate.

The build-up characteristics of the specific intensity of phosphorescence depend on the excitation density. As an example, the calculated specific intensity of the λ_3 -component of phosphorescence as a function of excitation time for five different excitation densities are shown in Fig. 18, compared with the observ-

ed intensity of the λ_3 -component of phosphorescence. Because the specific intensity of phosphorescence was used instead of the intensity of phosphorescence for the calculated values, the absolute value of $J_1 B_1 = 30 \text{ sec}^{-1}$ for the curve which show a good agreement with observed values does not seem to be correct. The validity of the theory mentioned above, however, seems to be supported by this result. The observed decay constant of $\tau_3 = 3.87 \text{ hr}$ at $297\text{--}298^\circ\text{K}$ is in complete agreement with the calculated value of $\tau_3 = 3.867 \text{ hr}$ at 300°K , as mentioned before. The other components of phosphorescence observed here will be attributed to the transitions omitted in Fig. 1, as suggested before.

(XII) Intensity of fluorescence

The fundamental equation of luminescence given by Eq. (8) and the specific intensity of fluorescence given by Eq. (17) concern themselves with the properties of the thin layer having a thickness of dx in which the excitation density is considered to be constant, as mentioned before. The actual layer or crystal of phosphor, however, has a finite thickness through which the excitation density is decreased with the depth of penetration by the absorption or scattering of exciting radiation. We must, therefore, integrate the specific intensity of fluorescence with respect to thickness of the phosphor layer, considering the effect of absorption and scattering of radiation, in order to obtain the intensity of fluorescence.

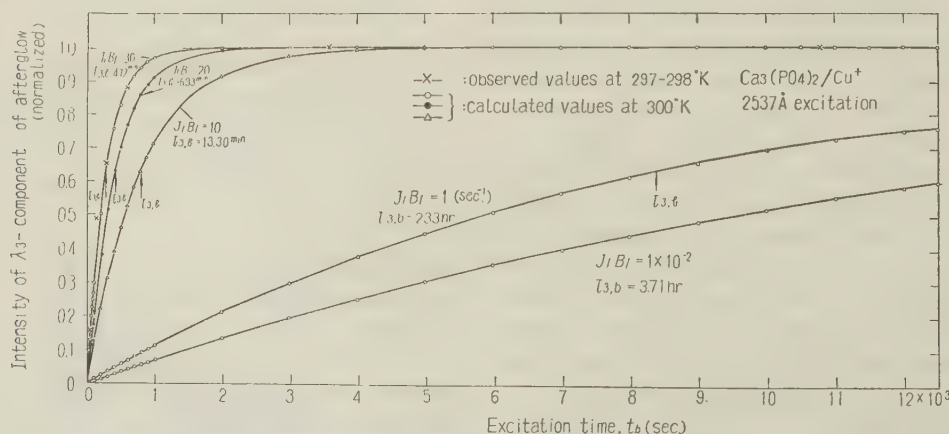


Fig. 18. Calculated build-up curves of λ_3 -component of afterglow are compared with the observed values for λ_3 -component of Cu-activated β -calcium orthophosphate excited with strong 2537 Å at $297\text{--}298^\circ\text{K}$. The calculated curves deal with the specific intensity of phosphorescence at 300°K , while the observed values with the intensity of phosphorescence.

Let us first consider a large single crystal of phosphor which is under steady excitation by ultraviolet radiation. The absorption coefficient of the phosphor activated with impurity atom, α , will be expressed by

$$\alpha = \alpha_1 + \alpha_i = \sigma_1 n_0 + \sigma_i (n^+ - n_0), \quad (12.1)$$

where α_1 and α_i are respectively the absorption coefficient for the activators and host crystal, σ_1 and σ_i are respective absorption cross sections, and n_0 and n^+ are the number of activators and positive ions involved in the unit volume of crystal, respectively, assuming that the activators are introduced in the matrix replacing the positive ions.

Neglecting the surface reflection of the incident radiation, the energy density of excitation at a depth of x is given by

$$J_1(x) = J_1 \cdot e^{-\alpha x}, \quad (12.2)$$

where J_1 is the energy density of the incident exciting radiation on the surface. Taking into account the correction factor τ for the reflection of the exciting radiation and fluorescent light and for the geometry of measurement, the specific intensity of fluorescent light which is produced in the thin layer of thickness dx at depth x and emitted from the front surface of crystal is given by, according to Eqs. (19) and (12.2),

$$dI_{2,f}(x) = \frac{a \cdot J_1 B_1 \cdot e^{-\alpha x} \cdot e^{-\alpha_f \cdot x}}{b + d \cdot J_1 B_1 \cdot e^{-\alpha x}} dx, \quad (12.3)$$

where α_f is the absorption coefficient for fluorescent light. The same form as Eq. (12.3) will hold for the case of powdered phosphor layer. For Cu-activated β -calcium orthophosphate, the values of constants, a , b and d , in Eq. (12.3) are given by

$$a = n_0 A_2 \pi_3 \pi_4 \pi_5, \quad b = \pi_5 (\pi_2 \pi_3 \pi_4 - \pi_2'' \pi_3 k_4'' - k_2'' k_3'' \pi_4),$$

and

$$d = \pi_2'' \pi_3 \pi_4 + \pi_5 (\pi_3 \pi_4 + k_2'' \pi_4 + \pi_2'' \pi_3). \quad (12.4)$$

Considering that α_f is usually much smaller than α , we can obtain from Eq. (12.3) the following results by integration under various conditions:

(12.a) General case

$$I_{2,f}(l) = \frac{\tau}{\alpha + \alpha_f} \cdot \frac{a}{d} \left[\ln \left(1 + \frac{J_1 B_1}{b} \right) - \ln \left\{ 1 + \frac{J_1 B_1}{b} \cdot e^{-(\alpha + \alpha_f) \cdot l} \right\} \right], \quad (12.5a)$$

$$I_{2,f}(\infty) = \frac{\tau}{\alpha + \alpha_f} \cdot \frac{a}{d} \cdot \ln \left(1 + \frac{d \cdot J_1 B_1}{b} \right), \quad (12.5b)$$

(12.b) $d \cdot J_1 B_1 / b \ll 1$

$$I_{2,f}(l) = \frac{\tau}{\alpha + \alpha_f} \cdot \frac{a \cdot J_1 B_1}{b} \{ 1 - e^{-(\alpha + \alpha_f) \cdot l} \}, \quad (12.6a)$$

$$I_{2,f}(\infty) = \frac{\tau}{\alpha + \alpha_f} \cdot \frac{a \cdot J_1 B_1}{b}, \quad (12.6b)$$

where l denotes the effective thickness of the phosphor layer. In our case, we can consider that the effective thickness of the phosphor layer is practically infinite.

The absorption coefficient α_1 for β -calcium orthophosphate activated with 0.5 mol % Cu is estimated to be of the order of 10^2 cm^{-1} for 2537Å. Since the crystal of this phosphor contains about 3×10^{-19} Cu⁺ ions per unit volume, the absorption cross section of the activator center for 2537Å is estimated to be about $3 \times 10^{-18} \text{ cm}^2$. Assuming that the flux density of 2537Å radiation of moderate intensity is, for the sake of convenience, about 3×10^{15} photons $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (11), we have

$$J_1 B_1 = 3 \times 10^{-18} \times 3 \times 10^{15} \approx 1 \times 10^{-2} \text{ sec}^{-1}. \quad (12.7)$$

For Cu-activated β -calcium orthophosphate, the values of d/b at various temperatures are smaller than 2.3. Therefore, the value of $d \cdot J_1 B_1 / b$ is about 2×10^{-2} or less for the ordinary excitation density of 2537Å. Thus Eq. (12.6b) holds in our case.

(XIII) *The Relation between the fluorescent efficiency and concentration of activator (concentration quenching)*

According to Eq. (12.6b), we can express the fluorescent efficiency of the phosphor excited with 2537Å by

$$\varepsilon_{2,f} = \frac{I_{2,f}}{\tau \cdot n_{2,1}} = \frac{a}{b} \cdot \frac{\sigma_1}{\alpha + \alpha_f} = \eta_{2,f} \cdot \frac{n_0 \cdot \sigma_1}{\alpha + \alpha_f}. \quad (13.1)$$

If we neglect α_f compared with α , we have, according to Eq. (12.1),

$$\varepsilon_{2,f}(c_0) = \eta_{2,f}(c_0) \cdot \frac{c_0}{c_0 + \sigma_1/\sigma_1 \cdot (1 - c_0)} \quad (13.2)$$

with

$$c_0 = \frac{n_0}{n^+}. \quad (13.3)$$

According to Eq. (1.3), the quantum efficiency of fluorescence will be expressed as a function of concentration of activators by

$$\eta_{2,f}(c_0) = \frac{1}{1 + \frac{k_2'}{A_2} + \frac{A_2'(c_0) + k_2'''}{A_2} \cdot \left(1 - \frac{k_4'''}{\pi_4}\right) + \frac{k_2''}{A_2} \left(1 - \frac{k_3'''}{\pi_3}\right)}. \quad (13.4)$$

In this equation, it was assumed that A_3' and A_4' were independent of the concentration of activators because of their small values compared with A_2' . As it has already been explained, the term $A_2'(c_0)$ is considered as expressing the probability of the dipole-quadrupole energy transfer from emitting state 2 to quenching state 4 between activator centers. Using the transition probability due to (d - q) interactions given by Dexter⁽¹²⁾, the averaged transition probability $P(d \cdot q)$ was calculated. Assuming a homogeneous distribution of activators in the matrix, it follows that

$$P(d \cdot q) = \frac{3}{5} \cdot \frac{\gamma^{8/3}}{\tau_s} \left\{ \frac{n_0}{v_0^{5/3}} + \frac{3}{2} \cdot \frac{n_0}{v_0^{2/3}} + \frac{3}{2} \cdot n_0^{8/3} \cdot e^{2n_0 v_0} \cdot \Gamma\left(\frac{1}{3}, n_0 v_0\right) \right\}, \quad (13.5)$$

where v_0 is the volume excluded by the presence of an activator and the notation of γ and τ_s is the same as that given by Dexter⁽¹²⁾.

Now, let Z be the number of positive ion sites to which an activator can transfer excitation energy, then we have

$$A_2'(c_0) = c_0 Z \cdot \overline{P(d \cdot q)}. \quad (13.6)$$

Substituting the values of $v_0 = 1 \times 10^{-21} \text{ cm}^3$, $1/\tau = 3.92 \times 10^2 \text{ sec}^{-1}$, $1/\tau_s = 1.14 \times 10^6 \text{ sec}^{-1}$, $E = 2.57 \text{ eV}$ and assumed value of $1/7 \text{ eV}$ for the maximum value of the overlap integral involved in γ into Eq. (13.6), we have $Z = 8.3$ and $\gamma = 1.3 \times 10^{-20} \text{ cm}^3$. This value of Z is close to the number of the nearest like neighbours and seems to be reasonable. Substituting the relation (13.6) into Eq. (13.4), we can calculate the concentration dependence of $\eta_{2,f}(c_0)$. Then, according to Eq. (13.2), the relation between the fluorescent efficiency and concentration of activators can be calculated, if the ratio of σ_1/σ_1 is known. It was

determined so that position of the maximum point of the calculated values coincided with that of observed values, as shown in Fig. 19, and it was

$$\sigma_1/\sigma_1 = 7 \times 10^{-4}. \quad (13.7)$$

This value seems to be reasonable and calculated result shown in Fig. 19 is also satisfactory considering the large fluctuation of experimental values

Using Eq. (12.5b), we can now calculate the temperature dependence of fluorescent intensity for the phosphor activated with 0.5 mol % Cu and under excitation by 2537Å of

various intensity. The calculated results are shown in Fig. 20. The calculated curves except extremely weak excitation show a minimum point whose depth increases with increasing excitation density. Since the measurement of the temperature dependence of fluorescent intensity was carried out under considerably weak excitation by $2537\text{\AA}$, which is estimated to be of the order of $J_1 B_1 = 1 \times 10^{-3} \text{ sec}^{-1}$ or less, the degree of agreement between the calculated and observed values

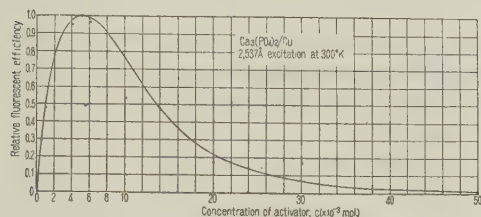


Fig. 19. Fluorescent efficiency of Cu-activated β -calcium orthophosphate excited with $2537\text{\AA}$ at 300°K as a function of the concentration of activators. Full line: calculated curve, $\circ$: observed value.

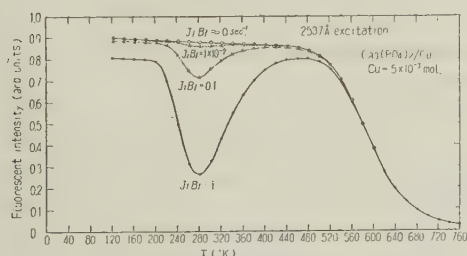


Fig. 20. Calculated temperature dependence of fluorescent intensity of β -calcium orthophosphate activated with 0.5 mole per cent copper and excited with $2537\text{\AA}$ of various intensities.

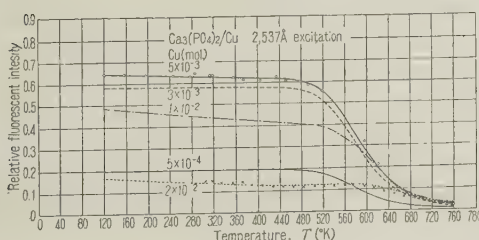


Fig. 21. Calculated temperature dependence curves of fluorescent intensity of β -calcium orthophosphate activated with various amounts of copper and excited with extremely weak $2537\text{\AA}$ radiation are compared with the observed values (marked with $\circ$ and $\times$).

is satisfactory, as clearly shown by the upper most curve in Fig. 21 which was reproduced from the corresponding curve in Fig. 20 and compared with the observed values. All curves shown in Fig. 21 were calculated under conditions subject to $J_1 B_1 \ll 1 \text{ sec}^{-1}$, and all curves except the uppermost curve were calculated using no adjustable parameters; the calculated results, therefore, are quite satisfactory.

Acknowledgements

The author wishes to express his sincere thanks to Dr. Tsuneo Harada, the Director of Matsuda Research Laboratory of Tokyo Shibaura Electric Co., for the continuous support and encouragement. This paper was read at the Annual Meeting of the Chemical Society of Japan, Tokyo, April 1-5 (1955), April 4-8 (1957), and Kyoto, April 2-6 (1956).

References

- 1) Y. Uehara, Y. Kobuke and I. Masuda: J. Electrochem. Soc. **106** (1959) 200.
- 2) S. Glasstone, K. J. Laidler and H. Eyring: *Theory of Rate Processes* (McGraw Hill Book Co., Inc., New York and London, 1941). F. E. Williams and H. Eyring: J. Chem. Phys. **15** (1947) 289.
- 3) R. Kubo and Y. Toyosawa: Proc. Theor. Phys. **13** (1955) 160.
- 4) W. De Groot: Physica **6** (1939) 275. G. R. Fonda: J. Appl. Phys. **10** (1939) 408.
- 5) c.f. H. W. Leverenz: *An Introduction to Luminescence of Solids* (John Wiley & Sons, Inc. New York, 1950) 262-278.
- 6) R. T. Ellickson: J. Opt. Soc. Amer. **36** (1946) 264.
- 7) F. E. Williams and H. Eyring: l.c.
- 8) G. S. Gessner: Phys. Rev. **36** (1930) 207.
- 9) W. Grother: Z. Phys. **112** (1939) 541. C. Hagen: Phys. Z. **40** (1939) 621. N. C. Beese and J. W. Marden: J. Opt. Soc. Amer. **32** (1942) 317.
- 10) P. Fröhlich and Z. Gulai: Z. Phys. **104** (1937) 549. L. Szalay: Acta. Chim. Phys. Univ. Szeged **2** (1948) 6; *ibid.* **2** (1950) 255. P. Fröhlich and L. Szalay: Research **2** (1949) 245.
- 11) H. W. Leverenz: loc. cit. p. 62.
- 12) D. L. Dexter: J. Chem. Phys. **21** (1953) 836; *ibid.* **22** (1954) 1063. Th. Förster: Ann. Physik **2** (1948) 55.

Germanium Crystal as a Neutron Monochrometer and the Determination of its Higher Order Contaminations*

By John T. WAJIMA,

Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo

Brice M. RUSTAD and Edward MELKONIAN

*Columbia University, New York, N. Y. and
Brookhaven National Laboratory, Upton, N. Y.*

(Received September 8, 1959)

In order to cover the wave length range $1\sim 4\text{\AA}$ with neutron crystal spectrometers, an attempt was made of using as a neutron monochrometer a germanium crystal. Germanium has a 'diamond cubic structure and the second order (222) reflection is theoretically forbidden. The intensity ratio of third to first order neutrons, I_3/I_1 , at thermal energy with a $1/v$, BF_3 counter was determined experimentally by a double crystal method using a second silicon crystal analyser, to be 0.023 ± 0.002 in agreement with the theoretically predicted values, $I_3/I_1=0.0245$ and $I_4/I_1=0.0055$. A maximum value of 0.2% was also measured for the second order contamination in the same way. The total higher order contamination determined from the transmission of pyrex glass plates was $(4.7\pm 0.5)\%$ at thermal energy, assuming only the third order contamination. The comparison of Ge, Si and NaCl crystals as monochrometers is discussed. The experiment indicates the successful use of a germanium crystal in $\text{\AA}$ region as a neutron monochrometer and also confirms the ways of determining higher order contaminations.

§ 1. Introduction

The basic condition upon which the interpretation of neutron crystal spectrometer data is based is that the coherent scattering of neutrons from single crystals is described by Bragg's law,

$$n\lambda = 2d \cdot \sin \theta \quad (1)$$

where

λ : de Broglie wave length, θ : Bragg angle,
 d : interplanar distance, n : order number

For any particular Bragg angle θ_0 , neutrons having wave lengths $\lambda_0, \lambda_0/2, \lambda_0/3, \dots, \lambda_0$ being equal to $2d \cdot \sin \theta_0$, will be reflected into a counter which is set at angle $2\theta_0$ with respect to the direction of neutrons from a reactor. The effect of these higher order contaminations will alter the observed quantities, transmissions in most cases, of a sample as a function of ratios of higher order intensities

to the first and of the cross section of a sample to be examined. Due to the fact that the neutron spectrum of the Brookhaven Reactor has its peak somewhere around 0.07 eV (about $1\text{\AA}$), it is extremely difficult to get the fairly good monochromatic neutron beam of the energy of about 0.025 eV ($1.8\text{\AA}$) with crystals like NaCl and LiF which have high reflectivities of the second order component, the energy of which falls near the peak of the pile spectrum. The use of crystals such as germanium and silicon which have a diamond cubic structure solved this problem as the second order reflection from (111) plane of those crystals is theoretically forbidden so that they could be used within some range below the peak of the Maxwellian distribution of neutrons from a reactor.

The use of a Ge crystal as a neutron monochrometer below $1\text{\AA}$ was mentioned by McReynold¹⁾, but no determination of higher orders, which were expected to be a great portion of the diffracted beam in this wave length region, was performed. He also mentioned that the second order (222) reflection

* This work was performed at Brookhaven National Laboratory from January to September, 1958, under the direction of Prof. W. W. Havens, Jr. of Columbia University, and was partially supported by the U. S. Atomic Energy Commission.

was less than 1% of the (111), using the spectrometer of Hasting and Corlisse.

The determination of higher orders by filter method was briefly described, for example, by Sturm²⁾. To determine the amount of higher orders with reasonable accuracy, a transmission type method similar to the filter method (we call this a pair-transmission method) was employed in this experiment, using a set of pairs of neutron absorbing material sheets. This method has an advantage over the filter method when the amount of the contamination is very small and the transmission values of the samples are hardly accurately determined at energies concerned with monoenergetic neutrons of those energies. At 1.8Å, in the present experiment, a pair of pyrex glass plates was used, and transmissions were measured both for a pair of plates together and for each plate separately. Transmission values for monoenergetic neutrons were calculated by an analytical method (Appendix 2).

The reflection from a forbidden plane was discussed by Renninger³⁾ in connection with X-rays and reproduced by James⁴⁾. He determined a structure factor of the (222) plane of the diamond, which is theoretically zero, using a number of diamonds of varying degrees of perfection and finding a very considerable variation in intensity. In the case of neutron diffraction, following his way of discussion, the limits between which the structure factor may lie will be widened due to the secondary extinction. But, at least, in analogy with X-ray diffraction, there must be some amount of the second order contamination from Ge crystals due to the imperfection of the crystals. In the present experiment this was determined by a newly devised double crystal method, using the second crystal as an analyser. The third order contamination was also determined in the same manner, and was compared with the values theoretically predicted.

§ 2. Theoretical Estimation of the Ratios of Higher Order Intensities to the First (Higher Order Contaminations)

Relative counting ratios of higher order components to the first order of Bragg-reflected neutron beams are governed by the reflectivities of each order reflection, by the neutron

spectrum from a pile and by the variation of counting efficiencies of particular neutron counters used.

Reflectivities of a crystal depend upon a number of factors such as;

- 1) The scattering and absorption cross sections of the constituent atoms.....attenuation factor and crystal structure factor.
- 2) The magnitude of the thermal agitation of these atoms.....Debye-Waller factor.
- 3) Crystallographic factors; interplanar distance, crystal thickness, mosaic spread, crystal structure factor, etc.

Since the cross section of the germanium crystal used for this experiment is of an unsymmetric oval shape and its (111) planes are neither perpendicular nor parallel to its surfaces*, the way of diffraction is neither reflection nor transmission type and the reflection of the neutrons is not symmetrical. Therefore, the calculation of reflectivities both for transmission and for reflection types on the ideal condition, symmetrical, is carried out and the mean values are employed for comparison with the experiment.

The complete expression of reflectivities of crystals is described as;

$$\mathcal{R}(\theta) = \exp(-2M) \cdot \mathcal{R}'(\theta) \quad (2)$$

where $\exp(-2M)$ is the Debye-Waller factor and $\mathcal{R}'(\theta)$ is the reflectivity of a crystal lattice.

The Debye-Waller temperature correction factor was discussed and justified by several authors⁵⁾. It is expressed as $\exp(-2M)$ where M is given by

$$M = \frac{6h^2}{mk\theta} \cdot \left(\frac{n}{2d}\right)^2 \cdot \left[\frac{1}{4} + \left(\frac{T}{\theta}\right)^2 \cdot Q\left(\frac{\theta}{T}\right)\right] \quad (3)$$

with

$$Q(z) = \int_0^z \frac{x}{e^x - 1} dx. \quad (4)$$

Here, θ is the Debye temperature of the crystal, h and k are Planck's and Boltzmann's constants, respectively, m is the nuclear mass, d is the grating space, n is the order number, and T is the temperature of the crystal in degrees Kelvin. The Debye temperatures of Ge, Si, and NaCl crystals were taken to be 390°K, 660°K, and 320°K⁶⁾, respectively. The function $Q(z)$ is given by Debye and reproduced in Blake's paper⁷⁾. The Debye-Waller factors for Ge, Si and NaCl thus calcu-

* See Fig. 1.

culated are given in Table I.

Expression of the reflectivity of a crystal lattice, $\mathcal{R}(\theta)$, have been derived by Goldberger and Seitz⁸⁾, and Bacon and Lowde⁹⁾. The results of Bacon and Lowde, which are the modification to neutrons, of the expression developed for X-rays by Zachariasen¹⁰⁾, are the most readily adaptable for computation purposes and the estimation calculated here was based upon their results. The reflectivity, $\mathcal{R}(\theta)$, is given, according to Bacon and Lowde, as the integrated reflection for an ideally imperfect crystal⁹⁾ in the form of integrals over the diffraction curves;

Reflection method:

$$\mathcal{R}(\theta)=\int_{-\infty}^{\infty}\frac{a\cdot d\Delta}{(1+a)+\sqrt{1+2a}\cdot\coth[A\sqrt{1+2a}]}$$

(5)

Transmission method:

$$\mathcal{R}(\theta)=\int_{-\infty}^{\infty}\sinh(Aa)\cdot\exp[-A(1+a)]\cdot d\Delta$$

(6)

where

$$A=\mu\,t_0/\gamma_0$$
$$a=(Q/\mu)\,W=(Q/\mu)[1/\eta\sqrt{2\pi}]\cdot\exp(-\Delta^2/2\eta^2)$$
$$Q=(\lambda^3N^2/\sin2\theta)F^2$$

with

- μ :

true absorption coefficient
- t_0 :

thickness of the crystal
- γ_0 :

direction cosine of the incident beam with respect to the inward normal to the plane
- N :

reciprocal of the unit cell volume
- F :

structure factor, which is given as

$$\sum_{\text{atoms}}\sqrt{\sigma_{\text{coh}}/4\pi}\cdot\exp[2\pi i(kx/a$$

$+ky/b+lz/c)]$

W : mosaic block angular distribution function, defined so that $W(\Delta)\cdot d\Delta$ is the fraction of mosaic blocks having their normals between the angles Δ and $\Delta+d\Delta$ to the normal to the crystal. $W(\Delta)$ is usually taken to be gaussian and is written as above with the standard deviation η .

η : mosaic spread

The expression for the reflectivity for the simplest case, i.e. symmetrical transmission, was derived by Holm¹¹⁾ from equation (6) and was also used for our computation. His result is

$$\mathcal{R}(\theta)=\sqrt{\pi/2}\cdot\eta\,e^{-A}\sum_{j=1}^{\infty}\frac{(r\tan^2\theta)^j}{\sqrt{j}\times j!}(-1)^{j+1}$$

(7)

where

$$r=\frac{8d^3\cdot t_0N^2F^2}{\sqrt{2\pi}\,n^3},$$
$$A=\mu\frac{t_0}{\gamma_0}=\left[\sum_iN_i(\sigma_{\text{at}}+\sigma_{\text{st}})\right]\frac{t_0}{\gamma_0}.$$

(8)

These general treatments of reflectivities have their most valuable applicability, according to Bacon and Lowde, when the crystal is medium in thickness and absorption, i.e.

$$50\frac{\eta}{Q}>\frac{t_0}{r_0}>\frac{1}{4}\frac{\eta}{Q}\quad\text{and}\quad4\frac{Q}{\eta}>\mu>\frac{1}{50}\frac{Q}{\eta},$$

(9)

where reflectivities can be approximated as parabolas, $\text{const}\times Q^{1/2}$, over the most part of the range. Beyond these limits, the reflectivity is simply expressed as $Q/2\mu$ for thin or absorbing crystals and is a steadily and slowly increasing function of Q for thick or non-absorbing crystals. Most of the crystals in practical use are medium in this respect.

Table I. Calculation of higher order contaminations.

Crystal (Plane)	n	e^{-2M}	$\mathcal{R}'\ (\times 10^{-3})$		$\mathcal{R}\ (\times 10^{-3})$		relative $\mathcal{R}$		relative I		thickness (cm)
			trans.	refl.	trans.	refl.	trans.	refl.	trans.	refl.	
Ge (111)	1	0.985	1.62	2.50	1.58	2.46	100	100	100	100	0.5
	3	0.870	0.145	0.262	0.126	0.228	8.0	9.3	2.3	2.6	
	4	0.782	0.124	0.218	0.097	0.170	6.1	6.9	0.50	0.60	
Si (111)	1	0.984	1.16	2.04	1.14	2.00	100	100	100	100	1.0
	3	0.863	0.064	0.131	0.055	0.113	4.8	5.7	1.4	1.6	
	4	0.770	0.054	0.116	0.042	0.090	3.7	4.5	0.32	0.38	
NaCl (200)	1	0.976	0.964	1.39	0.941	1.31	100	100	100	100	1.27
	2	0.907	0.348	0.464	0.316	0.421	33.6	32.1	50.0	47.7	
	3	0.803	0.116	0.233	0.093	0.187	9.9	14.3	2.9	4.1	

Table II. Crystal constants.

	Ge	Si	NaCl
η	1.45×10^{-3} radian (=5 min.)	1.45×10^{-3} radian (=5 min.)	1.164×10^{-3} radian (=4 min.)
lattice const.	5.6575×10^{-8} cm	$(5.43059 \pm 5) \times 10^{-8}$ cm	$(5.63874 \pm 2) \times 10^{-8}$ cm
d_{111}	3.2664 "	3.13535 "	*2.81937 "
N^2	3.0497×10^{43} cm $^{-6}$	3.89868×10^{43} cm $^{-6}$	3.1111×10^{43} cm $^{-6}$
Bragg angle for 1.79818 Å	15°58.62'	16°39.84'	18°35.78'

* refers to d_{200}

$\mathcal{R}(\theta)/\eta$ as a function of $(Q/\eta)(t_0/r_0)$ for different values of $\mu t_0/r_0$ and $(1/\eta)(Q/\mu)$ is given in Bacon and Lowde⁹⁾. Examples, thus calculated for Ge, Si and NaCl crystals are listed in Table I. From these, it is clearly seen that the third order reflectivity of Ge and Si crystals is of the same order of magnitude as the fourth, while the third order reflectivity of NaCl crystals is much less than the second. They also show that the second order reflectivity of NaCl crystals is much less than the second. Crystal constants used for the computation are also given in Table II.

Pile spectrum and counter efficiency

Now the pile spectrum is taken into account in order to get the relative intensities of each order to the first. The equation to be used for the determination of the relative intensities is:

$$\zeta_n = \frac{I(\theta_1) \text{ } nth \text{ order}}{I(\theta_1) \text{ } 1st \text{ order}} = \frac{I^*(\theta_n) \text{ } {}^n\mathcal{R}(\lambda_n) \text{ } {}^{13}\mathcal{R}^*(\lambda_1)}{I^*(\theta_1) \text{ } {}^1\mathcal{R}(\lambda_1) \text{ } {}^{13}\mathcal{R}^*(\lambda_n)} \quad (10)$$

where ${}^n\mathcal{R}(\lambda_m)$ represents a reflectivity of n th order reflection and of neutrons of wavelength λ_m , and asterisks denote the quantities related with a NaCl crystal mentioned below. The derivation of the equation is discussed in Appendix 1. The pile spectrum used in this estimation is the one previously measured¹²⁾ with a NaCl crystal. The result of theoretical estimation thus obtained about relative intensities is listed in the last column of Table I, which again shows the inferiority of NaCl crystals in this wave-length region.

$$\Delta\alpha = \Delta\beta/\sqrt{1-4\beta}$$

with

$$\Delta\beta = \beta \sqrt{\left[\frac{\Delta(\tau_{12} - \tau_1\tau_2)}{\tau_{12} - \tau_1\tau_2} \right]^2 + \left[\frac{\Delta({}_1T_3 - {}_1T_1)}{{}_1T_3 - {}_1T_1} \right]^2 + \left[\frac{\Delta({}_2T_3 - {}_2T_1)}{{}_2T_3 - {}_2T_1} \right]^2} \quad (12)$$

§ 3. Experimental Determination of Higher Order Contaminations by Pair-Transmission Method

(i) Principle of the method

Assume in the reflected beam there exists α of the lowest high order contamination, α being the ratio of the intensities of the lowest high order to the total, with counter efficiency included. Orders higher than the lowest contamination (3rd order in the case of a germanium crystal) are assumed to be zero. A set of pairs of samples of suitable thickness, a pair of pyrex glass plates and a pair of cadmium sheets in this experiment, was used and transmissions for a pair of samples together and for each sample separately were taken. Then α is calculated by the equation:

$$\alpha = \frac{1 - \sqrt{1 - 4\beta}}{2}$$

with

$$\beta = \frac{\tau_{12} - \tau_1\tau_2}{({}_1T_3 - {}_1T_1)({}_2T_3 - {}_2T_1)}, \quad (11)$$

when the lowest high order is the third. Here,

τ_{12} : experimentally measured transmission of two samples together

τ_1, τ_2 : experimentally measured transmissions of each sample separately

${}_i T_n$: analytically calculated transmission of i th sample for n th order neutrons

The derivation of this equation is discussed in Appendix 1 and the analytical calculation of transmissions of pyrex glass plates, in Appendix 2.

The error associated is;

By dividing the experimental values and the calculated into two independent groups in this way, errors associated with this kind of measurement were reduced to the minimum. By filter method, on the other hand, it is impossible to determine α with good accuracy due to the unbalance between the errors of transmission values calculated, T , and those experimentally measured, τ .

(ii) *Experimental arrangement and results*

The Columbia crystal spectrometer located at Brookhaven National Laboratory was used with a germanium crystal kindly supplied by the Bell Telephone Laboratories. The description of a high resolution neutron crystal electrometer of the similar kind is given by many authors¹³⁾. The schematic description of the experimental arrangement is shown in Fig. 1. Details of samples used at various energies

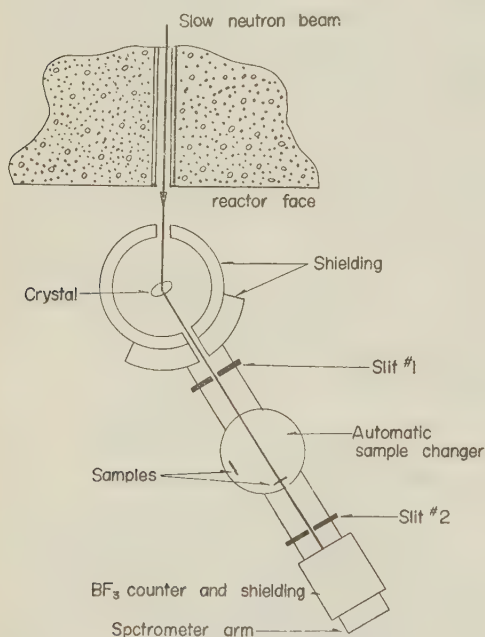


Fig. 1. Schematic description of the experiment of pair-transmission method.

Table III. Samples used for the order determination by pair-transmission method.

Samples	Thickness	Length	Width
P.G. Plate # 800	(.9650 $\pm$ 5.1) mm	$\sim$ 100mm	$\sim$ 38mm
# 900	(.9510 $\pm$ 5.5)	"	"
#1000	(.9859 $\pm$ 5.4)	"	"
Cd sheet # 1	(.508 $\pm$ 36)	"	"
# 2	(.0953 $\pm$ 25)	$\sim$ 50	$\sim$ 25

are given in Table III. The fractions of the third order thus determined between 1.8Å and 1Å are graphically shown in Fig. 2. The main source of the errors was the one from the accuracy of transmission values of samples and the careful attention was paid to measure transmissions as accurately as possible. The counter used was a $1/\nu$, Nancy Wood, enriched BF_3 counter and was used with its center line in a vertical plane and at 45 degrees with respect to the neutron beam. As shown in Fig. 2, α is minimum around 0.07 eV, peak of the pile spectrum, and increases with decreasing energy.

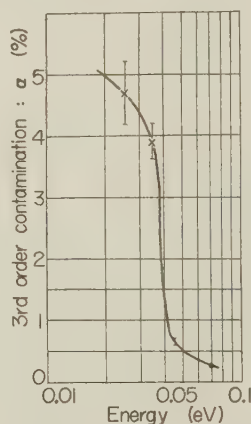


Fig. 2. 3rd order contamination (determined by pair-transmission method).

$$\alpha \equiv \frac{I(\theta) \text{ 3rd order}}{I(\theta) \text{ total}}$$

§ 4. Experimental Determination of Higher Order Contaminations by Double Crystal Method

(i) *Principle of the method*

The quantity we can define directly from measurements described in the last chapter is the intensity ratio of the lowest high order to the total with the counter efficiency included and is on the assumption that the contribution from all the higher orders higher than the lowest is zero or act as if they were from the lowest high order. Also though theoretically prohibited, the second order from the germanium crystal was not experimentally proved to be zero. By double crystal method, however, in principle, we can define, separately, each of the ratios of the higher orders to the first, and thus we can define or set the limit of second, third, —, order contaminations, respectively.

In order to determine the ratio of the n th order to the first, the spectrometer arm was set at angles $2\theta_a$ and $2\theta_b$ according to the condition shown in Appendix 1 and the counting ratios both for reflected and for through systems were taken simultaneously at angles $2\theta_a$ and $2\theta_b$, respectively. The second crystal on the arm is to analyze the beam reflected by the first crystal, and was set at the fixed angle $2\theta_n$ so as always to reflect selectively the n th order neutrons of the interested wavelength.

Then from Appendix 1, we finally get,

$$\zeta_n = \frac{I(\theta_b) \text{ } n\text{th order}}{I(\theta_b) \text{ 1st order}} = \frac{I(\theta_b) \text{ reflected}}{I(\theta_b) \text{ through}} \cdot \frac{I(\theta_a) \text{ through}}{I(\theta_a) \text{ reflected}} \cdot \frac{T_i^*(\lambda_1)}{T_i^*(\lambda_n)} \quad (13)$$

where $T_i^*(\lambda_1)$ and $T_i^*(\lambda_n)$ are the transmissions through the second crystal of "the through beam" of neutrons having first order wavelengths of λ_1 and λ_n , respectively.

(ii) Experimental arrangement and results

As the second crystal to analyse the beam reflected by the first crystal, a silicon single crystal of symmetric reflection type with its (111) plane parallel to its surfaces was used. This crystal was loaned through the courtesy of Dr. Sid Abrahams of Bell Tel. Laboratories, and was mounted on a conventional X-ray goniometer, which was fixed to the spectrometer arm. The counter used to measure the neutron intensity reflected by the

second crystal, was the same that was used for the contamination determination by the pair-transmission method and was set with its center line perpendicular to the reflected beam. The counter was shielded by Cd and paraffin and placed on a ply-wood board which was fixed to the spectrometer arm. The schematic description of the experiment is shown in Fig. 3. The counting ratios of both reflected and through beams were measured at the same time, and the relative transmissions were calculated from the through beam counting ratios and from the pile spectrum measured with the same crystal. The results of the measurements both for second and third order determinations were summarized in Table IV.

Table IV. Summary of the results at $1.8\text{\AA}$.

Methods	n	α	ζ_n (with NW counter)
Pair-transmission	3rd + 4th + ...	0.047 ± 5	0.049 ± 5 (converted)†
*Calculation	3rd 4th		0.0245 0.0055
Double X'tal	(2nd) _{max} 3rd		0.002 $0.023 \pm 2^{**}$

* Calculated values are the mean values between transmission and reflection types with the mosaic spread of 5 min. and with the thickness of 0.5 cm.

** (2nd)_{max} is included in the error.

† Here, α and ζ_3 are related by the equation

$$\zeta_3 \equiv \frac{I(\theta) \text{ 3rd order}}{I(\theta) \text{ 1st order}} = \frac{\alpha}{1 - \alpha} \quad (15)$$

The backgrounds were taken by twisting the first crystal, instead of the second, by about two degrees, since the goniometer on which the second crystal was mounted was not elaborately made enough to repeat taking the background with reasonable reproducibility of the peak counting rate. The net counting ratio of the reflected system for the measurement of the second order contamination was about five per cent of the background.

This second order contamination is to be included in the error associated with the determination of the third order contamination, as explained later.

§ 5. Discussion

The results at $1.8\text{\AA}$ are summarized and

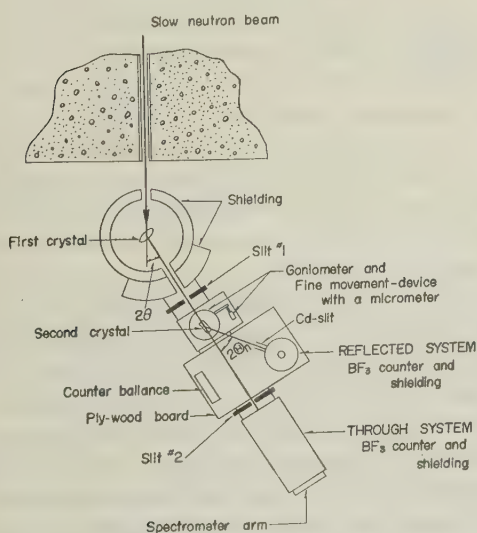


Fig. 3. Schematic description of the experiment of double-crystal method.

listed in Table IV for discussion.

The agreement between the value determined by double crystal method and the one calculated is excellent.

The difference between the two values of ζ_3 , third order contamination, obtained with *NW* counter by pair-transmission and by double crystal methods seems great but the value of ζ_3 determined by the former method is the one converted from the value of α which includes the contributions from all the higher orders higher than the 3rd order and this fact would make the value of ζ_3 determined by the transmission method much bigger than the value determined by the double crystal method. This can be easily seen, for example, by the following analysis:

Let α_n denote a intensity fraction of n th order, then from the similar discussion as in Appendix 1 and neglecting the product terms of α_n , it follows:

$$\tau_{12} - \tau_1 \cdot \tau_2 = \sum_n \alpha_n ({}_1T_{n-1} T_1) ({}_2T_{n-2} T_1), \quad n=3, 4, 5, \dots \quad (14)$$

Since

$$({}_1T_3 - {}_1T_1) ({}_2T_3 - {}_2T_1) < ({}_1T_4 - {}_1T_1) ({}_2T_4 - {}_2T_1) < \dots,$$

small values of α_4 and α_5 and so forth would form a great portion of the contribution to $(\tau_{12} - \tau_1 \cdot \tau_2)$. For instance,

$$\begin{cases} \alpha_3 = 0.025 \\ \alpha_4 = 0.006 \\ \alpha_5 = 0.003 \\ \alpha_7 = 0.002 \end{cases} \quad (15)$$

will yield the same value of $(\tau_{12} - \tau_1 \cdot \tau_2)$, as α_3 of 0.047 does when, in the latter, only the 3rd order is assumed to exist in reflected beams. This will prove the validity of the way of determining higher order contamination by the double crystal method and also checked the accuracy of the measurement which was done by the pair-transmission method. With an appropriate choice of the second crystal it is thus possible to determine or estimate by the double crystal method the fractions of higher order reflections separately with reasonable accuracy together with the pair-transmission method. In most cases in this wavelength region, where cross sections do not vary so rapidly, it may be appropriate to take (0.047 ± 5) as a fraction of third order

to the total with counter efficiency included on condition that there are only first and third order reflections.

The second order reflection, or the maximum limit of the second order as discussed in the following, is 0.2% against the first at 1.8Å, where we expect the maximum fraction of the second order neutrons, i.e. neutrons of the wavelength of 0.9Å, which falls near the peak of the pile spectrum. Since a part of, or the most of the net count was due to the incoherent scattering and as, because of the statistical accuracy and others, we could not distinguish clearly between those coherently and incoherently scattered neutrons, this value is to be regarded as the maximum limit of the second order reflection at 1.8Å. This, also, is to be included in the error associated with the determination of the third order contamination.

The limit of the applicability of this double crystal method to the determination of individual higher orders is due to the fact that the Bragg angle becomes so small as the order number increases that it gets impossible to place a shielded counter of the reflected system without interfering the though beam.

Besides below the maximum of the pile spectrum, this Ge crystal seems excellent also in eV range from the point of view of intensity and higher-order contamination as confirmed by experiments which are not discussed here.

Thus the germanium crystal was shown to be much superior to crystals such as sodium chrolide in intensity and order contamination. The only drawback of the former is that the half maximum width of its rocking curve is, for instance, about 5 min. and this seems the only disadvantage of the germanium crystal for programs such as automatic arm advance and so forth. To increase the mosaic spread is desirable from this point of view. This may increase the forbidden second order reflection but at the same time increase the first order reflectivity and decrease the fraction of 3rd, 4th, 5th, ... order reflections.

The variation of order contaminations and also of intensity with thickness, basing upon the theory of Bacon and Lowde, calculated for germanium and silicon crystals in the same manner as done in Table I is also shown in Figs. 4 and 5. The result for NaCl crystal

listed in Table I is also illustrated in the same figure for comparison. The mosaic spread of Ge and Si was arbitrarily but reasonably chosen to be 5 min. (1.454×10^{-3} radian), and that of NaCl, 4 min. (1.164×10^{-3} radian).

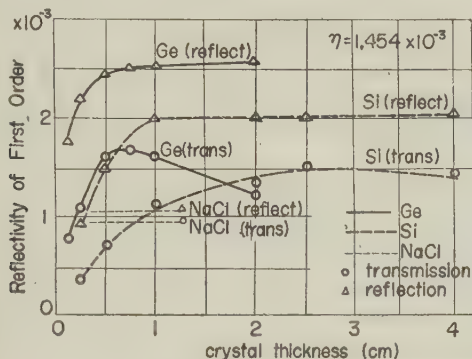


Fig. 4. Variation of reflectivity of first order.

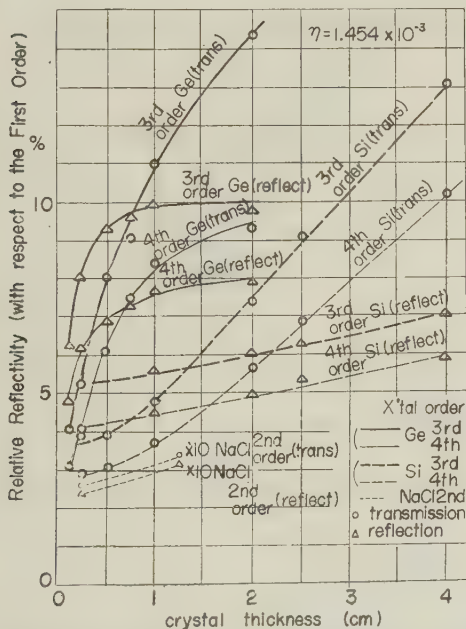


Fig. 5. Variation of relative reflectivity of higher orders.

Whether transmission type or reflection type is employed depends on the type and the purpose of experiments, but if we use the transmission type we may say, in conclusion, that a germanium crystal of the thickness of about 0.25 cm and a silicon crystal of the thickness of about 1 cm have roughly the same reflectivity and the same higher order contamination of about five per cent third order (in relative to the first) for the same mosaic spread. In both cases the increase of

the mosaic spread is desired. Down beyond these thicknesses their reflectivities are expected to drop down very rapidly.

The experiments with symmetric diffractions are hoped to be done to compare their results directly with the values theoretically calculated.

The result of the present experiment shows the possibility of the accurate measurements of cross sections exactly at $1.8 \text{ \AA}$ (0.0253 eV) with neutron crystal spectrometers, which has been impractical due to the higher order contamination associated with commonly used crystals. With some large single crystals as filter, which would shift the peak of the pile spectrum, or by a double crystal method, using an appropriate combination of crystals, it should be possible to extend the useful range of the spectrometers to longer wavelength region down beyond $1.8 \text{ \AA}$ to $4 \text{ \AA}$.*

§ 6. Conclusion

Assuming that there are only first and third order reflections from the (111) plane of a germanium crystal, the third order contamination was accurately determined between $1 \text{ \AA}$ and $1.8 \text{ \AA}$ by the pair-transmission method and was cross-checked by the double crystal method, resulting with $(4.7 \pm 0.5)\%$ third order contamination at $1.8 \text{ \AA}$ with counter efficiency included. The intensity ratio of third to first order neutrons, I_3/I_1 , at thermal energy with a $1/v$, BF_3 counter was determined experimentally by the double crystal method using a second silicon crystal analyser to be 0.023 ± 0.002 . This agrees very well with the value

* After Wajima's departure from Brookhaven a quartz filter composed of six 2-inch single crystals was used to further reduce order contamination, as suggested by Brockhouse at Calk River.

At thermal energy, the order contamination measured in the filtered beam is $I_3/I_1 = 3.7 \pm 0.7 \times 10^{-4}$ and $I_2/I_1 \leq 2.1 \times 10^{-4}$ to be compared with the values $3.2 \pm 0.3 \times 10^{-4}$ and 1.8×10^{-4} , respectively, computed from the known transmission of the quartz filter¹⁵⁾.

Further, with an improved neutron velocity selector¹⁶⁾, the germanium was shown to be used down to $3.5 \text{ \AA}$, beyond which the crystal is replaced by a mica crystal down to $12 \text{ \AA}$. Thus, the useful range of the neutron crystal spectrometer was extended continuously from $1 \text{ \AA}$ to $12 \text{ \AA}$, with suitable crystals and filters, with the higher order contamination of less than 0.5 per cent¹⁷⁾.

theoretically predicted.

The second order reflection, which is theoretically prohibited, was also determined to be less than 0.2% by the double crystal method.

The experiment indicates the successful use of a germanium crystal in Å region as a neutron monochrometer and also confirms the ways of determining higher order contaminations.

Acknowledgements

The authors gratefully express their appreciation to Prof. W. W. Havens, Jr. of Columbia University, who kindly gave Wajima the honour of joining the spectrometer program and encouragingly took active interest in the experiment. We wish to thank Dr. V.

Sailor and Dr. L. Hasting of Brookhaven National Laboratory and T. Prince of Bell Telephone Laboratories for their valuable suggestions and discussions. Thanks are also due to Dr. F. Gould, Dr. G. Moore and Dr. G. Safford for their helpful discussions and other. The authors also wish to thank Mr. R. Graeser and Miss A. Ripoli for their assistance in taking data, and also to thank people at the Computer Center for their handling the data.

The authors' profound appreciation is also due to those of Japan Atomic Energy Bureau and of Hitachi, Ltd., who were concerned with the atomic energy development program which enabled Wajima to work at Columbia University and Brookhaven National Laboratory.

Appendix 1. Equations used for Higher Order Contamination Measurements

Define:

- $I(\theta)$: Counting ratio detected by a counter
- $\epsilon(\lambda)$: Efficiency of the counter
- ${}^n\mathcal{R}(\lambda)$: Reflectivity of the crystal
- ${}^nR(\lambda)$: Resolution function of the spectrometer
- $\mathcal{S}_\lambda(\lambda)$: Intensity density: Intensity per unit wave-length from a pile
- n : refers to n th order.

Then,

$$I(\theta) = \sum_{n=1}^{\infty} \int_{\lambda'} \mathcal{S}_\lambda(\lambda_n) \cdot {}^n\mathcal{R}(\lambda_n) \cdot \epsilon(\lambda_n) \cdot {}^nR(\lambda' - \lambda_n) d\lambda'.$$

Now the function $\mathcal{S}_\lambda(\lambda_n) \cdot {}^n\mathcal{R}(\lambda_n) \cdot \epsilon(\lambda_n)$ is a slowly varying function of λ at λ_n and the equation can be rewritten

$$I(\theta_1) = \sum_{n=1}^{\infty} \mathcal{S}_\lambda(\lambda_n) \cdot {}^n\mathcal{R}(\lambda_n) \cdot \epsilon(\lambda_n) \cdot \Delta\lambda_n(\theta_1)$$

where $\Delta\lambda_n(\theta_1)$ is a half maximum width of the resolution function for n th order at angle θ_1 . Therefore,

$$\zeta_n \equiv \frac{I(\theta_1) \text{ } n\text{th order}}{I(\theta_1) \text{ 1st order}} = \frac{\mathcal{S}_\lambda(\lambda_n) \cdot {}^n\mathcal{R}(\lambda_n) \cdot \epsilon(\lambda_n) \cdot \Delta\lambda_n(\theta_1)}{\mathcal{S}_\lambda(\lambda_1) \cdot {}^1\mathcal{R}(\lambda_1) \cdot \epsilon(\lambda_1) \cdot \Delta\lambda_1(\theta_1)}.$$

If the pile spectrum is measured previously as; (* refers to the quantities related to this previous measurement)

$$\frac{I^*(\theta_n)}{I^*(\theta_1)} = \frac{\mathcal{S}_\lambda(\lambda_n) \cdot {}^1\mathcal{R}^*(\lambda_n) \cdot \epsilon^*(\lambda_n) \cdot \Delta\lambda_n(\theta_n)}{\mathcal{S}_\lambda(\lambda_1) \cdot {}^1\mathcal{R}^*(\lambda_1) \cdot \epsilon^*(\lambda_1) \cdot \Delta\lambda_1(\theta_1)}.$$

Then,

$$\frac{I(\theta_1) \text{ } n\text{th order}}{I(\theta_1) \text{ 1st order}} = \frac{I^*(\theta_n) \cdot {}^n\mathcal{R}(\lambda_n) \cdot {}^1\mathcal{R}^*(\lambda_1) \cdot \epsilon(\lambda_n) \cdot \epsilon^*(\lambda_1) \cdot \Delta\lambda_n(\theta_1)}{I^*(\theta_1) \cdot {}^1\mathcal{R}(\lambda_1) \cdot {}^1\mathcal{R}^*(\lambda_n) \cdot \epsilon(\lambda_1) \cdot \epsilon^*(\lambda_n) \cdot \Delta\lambda_n(\theta_n)}.$$

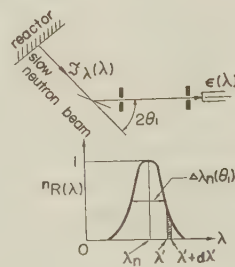


Fig. 6.

If the same counter is used for both measurements, and assuming

$$\frac{\Delta\lambda_n(\theta_1)}{\Delta\lambda_n(\theta_n)}=\frac{1}{\lambda_n},$$

we get

$$\zeta_n \equiv \frac{I(\theta_1) \text{ } nth \text{ order}}{I(\theta_1) \text{ } 1st \text{ order}} = \frac{I^*(\theta_n) \cdot n \Re(\lambda_n) \cdot \Re^*(\lambda_1)}{I^*(\theta_1) \cdot \Re(\lambda_1) \cdot \Re^*(\lambda_n)}.$$

Consider now that there are only first and third orders in the beam reflected by a crystal. Denote the counting ratio of the third order intensity to the total, α . Then, $\zeta_n=(\alpha/(1-\alpha))$

With the notation;

- τ_{12} : experimentally measured transmission of two samples together
- τ_1, τ_2 : experimentally measured transmissions of each sample separately
- T_n : analytically calculated transmission of i th sample for n th order neutrons

we can express, (See Fig. 7)

$$\left\{\begin{array}{l} \tau_1 = {}_1T_1 + ({}_1T_3 - {}_1T_1)\alpha \\ \tau_2 = {}_2T_1 + ({}_2T_3 - {}_2T_1)\alpha \\ \tau_{12} = {}_1T_1 \cdot {}_2T_1 + ({}_1T_3 \cdot {}_2T_3 - {}_1T_1 \cdot {}_2T_1)\alpha \end{array}\right.$$

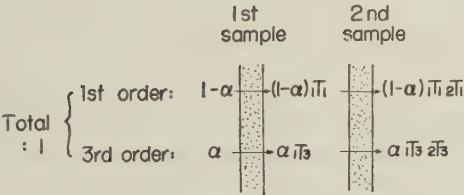


Fig. 7.

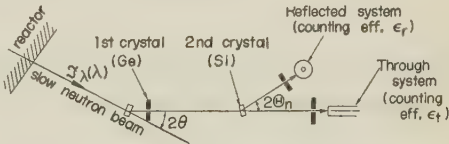


Fig. 8.

Therefore

$$\tau_{12}-\tau_1\cdot\tau_2=\alpha(1-\alpha)({}_1T_3-{}_1T_1)({}_2T_3-{}_2T_1),$$

and

$$\alpha=\frac{1-\sqrt{1-4\beta}}{2}$$

with

$$\beta=\frac{\tau_{12}-\tau_1\tau_2}{({}_1T_3-{}_1T_1)({}_2T_3-{}_2T_1)}.$$

Next is considered the double crystal method.

In order to determine the ratios of higher orders to the first, the spectrometer arm was set at angles $2\theta_a$ and $2\theta_b$ according to the conditions shown in App. Table I and the counting ratios both for through and reflected systems were taken simultaneously at angles $2\theta_a$ and $2\theta_b$, respectively. The second crystal on the arm is to analyze the beam reflected by the

App. Table I. Conditions of crystal angle setting for double crystal method.

Conditions	Crystals	The first order wavelength selectively reflected by the X'tal	Bragg angle
condition a	1st crystal	 λ_n	θ_a
	2nd crystal	 λ_n	θ_n (fixed)
condition b	1st crystal	 λ_1	θ_b
	2nd crystal	 λ_n	θ_n (fixed)

first crystal, and was set at the fixed angle $2\theta_n$ so as always to reflect selectively the n th order neutrons of the interested wavelength.

Then from conditions 'a' and 'b' we get

$$\frac{I(\theta_a) \text{ through}}{I(\theta_b) \text{ reflected}} = \frac{\mathfrak{Z}_\lambda(\lambda_n) \cdot {}^1\mathfrak{R}(\lambda_n)}{\mathfrak{Z}_\lambda(\lambda_n) \cdot {}^1\mathfrak{R}(\lambda_n)} \cdot \frac{T_i^*(\lambda_n)}{T_r^*(\lambda_n) \cdot {}^1\mathfrak{R}^*(\lambda_n)} \cdot \frac{\varepsilon_t(\lambda_n) \cdot \Delta_t \lambda_n(\theta_a)}{\varepsilon_r(\lambda_n) \cdot \Delta_r \lambda_n(\theta_a)}$$

and

$$\frac{I(\theta_b) \text{ reflected}}{I(\theta_b) \text{ through}} = \frac{\mathfrak{Z}_\lambda(\lambda_n) \cdot {}^n\mathfrak{R}(\lambda_n)}{\mathfrak{Z}_\lambda(\lambda_1) \cdot {}^1\mathfrak{R}(\lambda_1)} \cdot \frac{T_r^*(\lambda_n) \cdot {}^1\mathfrak{R}^*(\lambda_n)}{T_i^*(\lambda_1)} \cdot \frac{\varepsilon_r(\lambda_n) \cdot \Delta_r \lambda_n(\theta_b)}{\varepsilon_t(\lambda_1) \cdot \Delta_t \lambda_1(\theta_b)}$$

where intensities of through systems were approximated as those of the first order, r and t mean reflected and through systems, respectively, * refers to the second crystal, and T denotes transmission. Now from these two equations,

$$\begin{aligned} \xi_n &\equiv \frac{I(\theta_b) \text{ } n\text{th order}}{I(\theta_b) \text{ 1st order}} = \frac{\mathfrak{Z}_\lambda(\lambda_n) \cdot {}^n\mathfrak{R}(\lambda_n) \cdot \varepsilon_t(\lambda_n) \cdot \Delta_t \lambda_n(\theta_b)}{\mathfrak{Z}_\lambda(\lambda_1) \cdot {}^1\mathfrak{R}(\lambda_1) \cdot \varepsilon_t(\lambda_1) \cdot \Delta_t \lambda_1(\theta_b)} \\ &= \frac{I(\theta_b) \text{ reflected}}{I(\theta_b) \text{ through}} \cdot \frac{I(\theta_a) \text{ through}}{I(\theta_a) \text{ reflected}} \cdot \frac{T_i^*(\lambda_1)}{T_i^*(\lambda_n)}, \end{aligned}$$

where we assumed

$$\frac{\Delta_r \lambda_n(\theta_a) \cdot \Delta_t \lambda_n(\theta_b)}{\Delta_r \lambda_n(\theta_b) \cdot \Delta_t \lambda_n(\theta_a)} = 1.$$

Appendix 2. Principle of the Analytical Calculation of Transmissions of Pyrex Glass Plates

The procedure is to

- i) calculate $(n\sigma/G)$ from an analytical consideration
- ii) measure experimentally the density and thickness of samples and then determine G as the multiplication of those two.
- iii) from i) and ii), determine " $n\sigma$ " and transmission, which is equal to $\exp(-n\sigma)$

where

n : number of atoms per cm^2

σ : microscopic total cross-section

G : weight of the sample per cm^2

Define,

$$f_i = \frac{n_i A_i}{nA}, \text{ fractional weight of } i\text{th atoms}$$

and we get

$$n\sigma = \sum_i n_i \sigma_i = nA \sum_i \frac{f_i \sigma_i}{A_i} = GN_0 \sum_i \frac{f_i \sigma_i}{A_i}.$$

Therefore

$$n\sigma/G = N_0 \sum_i \frac{f_i \sigma_i}{A_i}.$$

In order to calculate the summation, we

divided it into two groups, i.e., the summation of absorption cross-section terms and that of scattering cross-section terms. In the latter the liquid effect was assumed to vary in the same way for each constituent element as for SiO_2 .¹⁴⁾

Now, using the result of chemical analysis of pyrex glass plates and the cross-section data¹⁸⁾,

$$\begin{aligned} n\sigma/G &= (0.90996 \pm .00301)\lambda \\ &\quad + (0.11776 \pm .00289)K \pm 0.0108 \end{aligned}$$

with

$$\begin{cases} \sigma_{\text{Babs}} = (420.4 \pm .3)\lambda \pm 5 \quad (\lambda \text{ in } \text{\AA}) \\ f_{\text{B}} = 0.1250 \pm .0004^* \\ f_{\text{Si}} = 0.8082 \pm .0005 \end{cases}$$

where f_{B} and f_{Si} are % weight of SiO_2 and B_2O_3 , respectively and

$$K \equiv K(\lambda) = \frac{\sigma_{\text{SiO}_2}(\lambda)}{\sigma_{\text{SiO}_2} \text{ at } 1.8 \text{\AA}}.$$

The densities of plates were measured by buoyancy method. They were found to be the same within experimental error, and as-

* The more precise measurement of transmission at $4.6 \text{\AA}$ shows that the boron content of each plate is the same within experimental error and, assuming f_{B} is common in all the plates, f_{B} is 0.12865 ± 0.0002 .

assuming the density is the same for all the plates, it was determined to be 2.2309 ± 0.0002 .

In order to measure thicknesses of the plates, we divided the 1 inch $\times$ 1/4 inch central area of each plate into eight regions, for each of which one measuring point was taken. Thicknesses were measured with a constant contact pressure type micrometer to the accuracy of 10^{-5} inch.

References

- 1) A. W. McReynold: Phys. Rev. **88** (1952) 958.
- 2) W. J. Sturm: Phys. Rev. **71** (1947) 757.
- 3) M. Renninger: Z. tech. Physik **16** (1935) 440.
- 4) R. W. James: *The Optical Principles of the Diffraction of X-rays* (G. Bell and Sons Ltd. London, 1950) 253 and 320.
- 5) P. Debye: Ann. Physik **43** (1914) 49. I. Waller: Ann. Physik **83** (1922) 154. F. C. Blake: Rev. Mod. Phys. **5** (1933) 169. R. Weinstock: Phys. Rev. **65** (1944) 1.
- 6) Handbuch der Physik Band 7, Teil-1, P. 362.
- 7) F. C. Blake: Rev. Mod. Phys. **5** (1933) 169.
- 8) M. L. Goldberger and F. Seitz: Phys. Rev. **71** (1947) 294.
- 9) G. E. Bacon and R. D. Lowde: Acta Cryst. **1** (1948) 303.
- 10) W. H. Zachariasen: *Theory of X-ray Diffraction in Crystals* (Wiley, 1944).
- 11) M. W. Holm: IDO-16115, March (1955).
- 12) BNL Memorandum (Oct. 18, 1957, B. Rustad et al) and others (unpublished).
- 13) L. B. Borst and V. L. Sailor: Rev. Sci. Instrum. **24** (1953) 141. V. L. Sailor et al: Rev. Sci. Instrum. **27** (1956) 26.
- 14) E. Melkonian: Phys. Rev. **76** (1949) 1744.
- 15) B. T. Rustad, J. T. Wajima and E. Melkonian: Reported at Amer. Phys. Soc. Meeting, Washington, D., C., April 30, May 1-2 (1959).
- 16) J. A. Moore, J. Rush and B. M. Rustad: Reported at Ame. Phys. Soc. Meeting, Washington, D., C., April 30, May 1-2 (1957). N. Holt: Rev. Sci. Instrum. **28** (1957) 1.
- 17) Private communication from Prof. W. W. Havens, Jr.
- 18) BNL-325 Second edition.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

Radiative Collisions between Molecular and Electron Beams, V. Angular Momentum Distributions of CH^* Separating from Simple Organic Molecules

By Tadao HORIE, Takayuki NAGURA
and Masamoto OTSUKA

Faculty of Science, Osaka University

(Received October 28, 1959)

Observations have been done of electron bombardments of the C_2H_2 , CH_2O and CH_3OH molecular jets in vacuum. The free radical $\text{CH}^*(B^2\Sigma^-)$ always shows a normal distribution of angular momentum. This experimental result is entirely different from the previous reports on the free radical $\text{OH}^*(2\Sigma^+)$ splitting from H_2O or H_2O_2 . For instance, the distribution curve for CH^* from C_2H_2 shows its maximum near $K=7$, while that for OH^* from H_2O_2 near $K=20$. This marked differences is discussed, and a statistical interpretation is also given of the angular momentum distribution for CH^* separating from C_2H_2 .

§ 1. Introduction

Several papers have so far been devoted in succession to studies of the rotational energy distribution amongst the OH^* radicals split by electron impact from their parent mole-

cules. In Part I⁽¹⁾⁻⁽⁸⁾, it has been shown that the angular momentum distribution for OH^* from H_2O exhibits a double maximum; the first or thermal maximum near $K=5$, and the second or abnormal one near $K=17$. In Part

II⁴⁾, the angular momentum distribution for OH* from H₂O₂ has been found to be further abnormal in appearance and to have a single maximum near $K=20$. In Part III⁵⁾, it has been seen that the OH* radical split from alcohols does not show any abnormal rotation, and the angular momentum distribution is quite similar to the Maxwell-Boltzmann distribution with a maximum near $K=7$. In Part IV⁶⁾, a theoretical interpretation has been proposed of the angular momentum distribution of OH* from H₂O₂ on the basis of the statistical theory and the predissociation of OH*.

In the present paper, to answer further questions about the rotational motion of the CH* radical separating from simple organic molecules, spectro-photometric measurements have been carried out of the rotational lines emitted by CH* split by electron impact from C₂H₂, CH₂O and CH₃OH.

§ 2. Experimental

Tank acetylene gas was used in the usual way to produce the molecular jet of C₂H₂ in vacuum. Similarly, the jet of CH₂O was ob-

tained by heating paraformaldehyde. The details of the experimental apparatus and procedure are all the same as described in the previous papers^{2), 3)}.

In Fig. 1 are presented the rotational intensity distributions for the λ 3872 CH band emitted by CH* split from CH₃OH, C₂H₂ and CH₂O, where the electronic state of CH* is $B^2\Sigma^-$. They are all normal and similar to the Maxwell-Boltzmann distribution for 2500°K. When compared with Fig. 3 in Part III⁵⁾, this experimental result tells us that the angular momentum distributions for CH* from simple organic molecules and those for OH* from alcohols are all more or less alike; they have their maxima near $K=7$. It should be mentioned here that the effective rotational temperatures for OH* from H₂O and H₂O₂, as shown in the previous papers¹⁾⁻⁴⁾, correspond to 14000 and 20100°K, respectively.

There may be several reasons why the CH* radical does not accept any appreciable energy of rotation in the dissociation processes of their parent molecules. For one thing, just before dissociation sets in, each of the parent molecules may not have enough excess potential energy to enhance the rotation of the free radical. For another, as discussed in the case of OH* from alcohols⁵⁾, multiple fragmentation of the parent molecule may prevent the free radical from getting a lot of energy of rotation, because the excess potential energy, even if it is sufficient, should be distributed to a variety of degrees of freedom.

In addition, there are indications that the molecular structure of the parent molecule may have a bearing on the angular momentum distribution shown by the free radical. For instance, the geometrical structure of C₂H₂ is a symmetric and linear form in contrast to a compact and bent one of H₂O₂. The marked difference between the angular momentum distribution for CH* from C₂H₂ and that for OH* from H₂O₂ will be dealt with in the following section.

Looking at the emission spectra shown in Fig. 2, a few comments may be made as follows. When C₂H₂ is subjected to the action of high-energy electrons (500 eV), the hydrogen Balmer lines come out as intensively as the CH bands do. This is in sharp contrast to the fact that the splitting of H₂O₂ by electron-

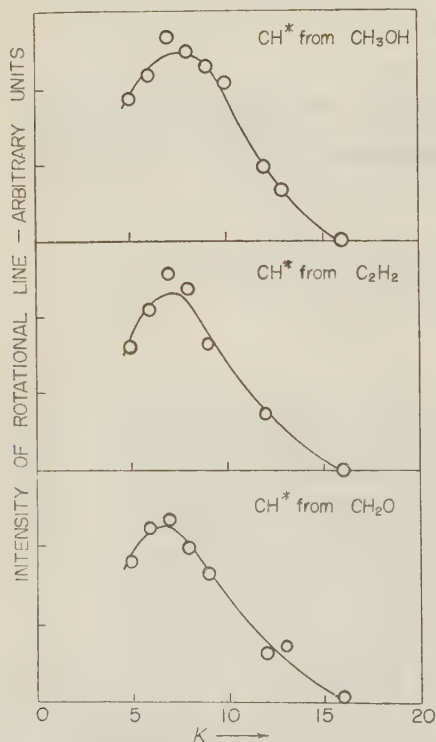


Fig. 1. The rotational intensity distributions for CH* split by electron-impact from CH₃OH, C₂H₂ and CH₂O.

impact is not accompanied with the emission spectra of these atomic lines, as shown in Part II⁴).

Referring to CH_2O , in addition to the atomic lines of H, the CO^+ comet-tail bands are also strongly observed. According to the mass-spectrometric study made for some organic compounds by A. Langer⁷⁾, there were observed, among the products of dissociation due to electron impact, fragments whose origin could not be accounted for by simple assumption of splitting established classical valence-bond lines of the compound, as is usually done in most cases of molecular decomposition. The occurrence of these rearrangement fragment radicals has been shown to be associated with the primary process of dissociation caused by the impinging electron, and further attributed to the intramolecular migration of hydrogens. In the case of such a simple molecule as CH_2O , however, any indication could not be recognized of the emission band spectrum of OH near 3064 Å.

By the way, in Fig. 3 is presented an ex-

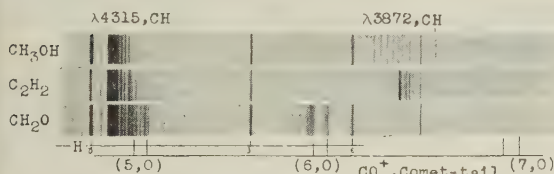


Fig. 2. The emission spectra from electron bombardments of molecular jets; from top to bottom, CH_3OH , C_2H_2 and CH_2O .

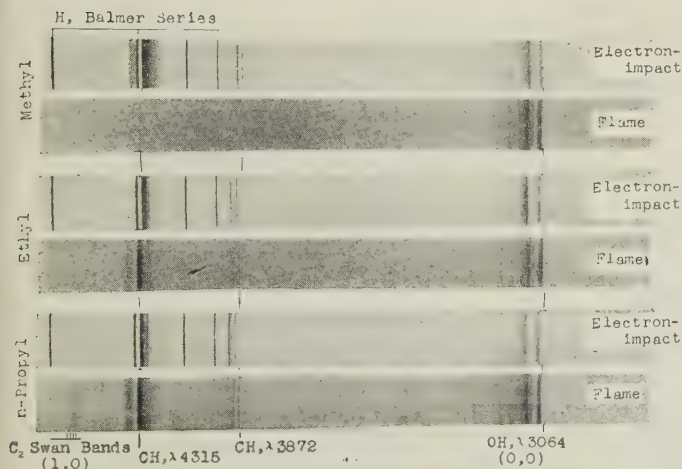


Fig. 3. The electron-impact and flame spectra for some alcohols.

ample to show how different the emission spectra obtained by our experimental method are from those of other light sources. The electron-impact spectra for some alcohols consist of the emissions from the free radicals, CH, OH and H, which can be expected by simple bond fission along classical valence lines, while the flame spectra do not contain the hydrogen Balmer series at all. Another example has already been presented in Part III;⁵⁾ the electron-impact and discharge spectra for some alcohols being compared with each other.

§ 3. Discussion

It is known that a linear symmetric form is given for the geometrical structure of the C_2H_2 molecule in the ground state⁸⁾. The valence electrons between the two carbons form a triple bond composed by a σ -bond and two π -bonds. The far ultraviolet absorption spectra of C_2H_2 studied by W. C. Price⁹⁾ has revealed that excitation of one of these valence electrons leads in general to the stable molecule in one of the excited levels designated as $np\Sigma$ and $np\Pi$, and further that strong predissociation of the lowest one of these excited levels causes the molecule to dissociate into normal CH radicals. Accordingly, the strong emission spectra of CH and H as shown in Fig. 2 must be due to some more violent excitation as, for instance,



In such a molecular dissociation, each of the free radicals, CH^* , C and H^* , may have an angular momentum around the center of mass of the whole system, and besides for the CH^* radical, the lighter particle H is circling the heavier one C. There is no reason why any of these angular momenta can be neglected, since the geometrical structure of C_2H_2 is not a compact form, but a linearly extended one. What is more, the two H atoms at the opposite ends of the C_2H_2 molecule may not be expected to have a chance to make any sufficient interaction with each other throughout the course of dissociation. Still,

the law of angular momentum conservation should be taken into consideration, in order to obtain a statistical distribution function for the rotational energy of CH^* .

A statistical interpretation for the angular momentum distribution of OH^* split from H_2O_2 has already been proposed in Part IV, where the law of angular momentum conservation is taken into consideration⁶⁾. However, the theoretical method proposed is reasonably applicable only to such a symmetric fragmentation as the splitting of H_2O_2 into two hydroxyl radicals. On the other hand, the C_2H_2 molecule makes an asymmetric and multiple fragmentation. Any attempt to

introduce the law of angular momentum conservation into a statistical theory for such a complicated process should be preceded by some fundamental studies on theoretical methods for more general use, as indicated by R. H. Milburn concerning the statistical theory of multiple meson production¹¹⁾.

At the present stage, without going further into discussion of the details of the dissociation process, we shall here simplify the calculation by considering only energy and linear momentum conservation. Then we have the phase volume for the range of rotational energy of CH^* extending from 0 to ε as follows,

$$\begin{aligned} \mathcal{V}(\varepsilon) = & h^{-11} \left[\prod_{i=1}^3 \iiint d^3 \mathbf{r}_i \iiint d^3 \mathbf{p}_i \right] \iint d\theta_1 d\phi_1 \iint dp_{\theta_1} dp_{\phi_1} \\ & \times \delta \left[E - \sum_{i=1}^3 (p_{xi}^2 + p_{yi}^2 + p_{zi}^2)/2m_i - (p_{\theta 1}^2 + p_{\phi 1}^2/\sin^2 \theta_1)/2A \right] \\ & \times \delta \left(\sum_{i=1}^3 \mathbf{p}_i \right) U[\varepsilon - (p_{\theta 1}^2 + p_{\phi 1}^2/\sin^2 \theta_1)/2A], \end{aligned}$$

where the subindices 1, 2 and 3 refer to CH^* , C and H^* , respectively, and where E is the excess potential energy possessed by the excited parent molecule. According to the Franck-Condon principle, E is nearly constant, since it is the vertical distance between the asymptotic plane of an upper repulsive surface of potential energy and the point reached after the quantum jump from the ground state, as shown in Fig. 7 in Part II⁴⁾.

The discontinuous functions have the Fourier representations

$$\delta(x) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\lambda \exp(i\lambda x),$$

and

$$U(y) = (2\pi i)^{-1} \int_{-\infty - i\Delta}^{\infty - i\Delta} d\alpha \alpha^{-1} \exp(i\alpha y), \quad (\Delta > 0).$$

Then we have

$$\begin{aligned} \mathcal{V}(\varepsilon) = & (2\pi)^{-5} h^{-11} i^{-1} \left[\prod_{i=1}^3 \iiint d^3 \mathbf{r}_i \iiint d^3 \mathbf{p}_i \right] \iint d\theta_1 d\phi_1 \iint dp_{\theta_1} dp_{\phi_1} \\ & \times \int_{-\infty}^{\infty} d\lambda \exp \left\{ i\lambda \left[E - \sum_{i=1}^3 (p_{xi}^2 + p_{yi}^2 + p_{zi}^2)/2m_i - (p_{\theta 1}^2 + p_{\phi 1}^2/\sin^2 \theta_1)/2A \right] \right\} \\ & \times \iiint_{-\infty}^{\infty} d^3 \boldsymbol{\mu} \exp \left(i\boldsymbol{\mu} \cdot \sum_{i=1}^3 \mathbf{p}_i \right) \int_{-\infty - i\Delta}^{\infty - i\Delta} d\alpha \alpha^{-1} \exp \{ i\alpha [\varepsilon - (p_{\theta 1}^2 + p_{\phi 1}^2/\sin^2 \theta_1)/2A] \}. \end{aligned}$$

By changing the order of integration, we have

$$\begin{aligned} \mathcal{V}(\varepsilon) = & \text{const.} \left[\prod_{i=1}^3 \iiint d^3 \mathbf{r}_i \right] \iint d\theta_1 d\phi_1 \int_{-\infty}^{\infty} d\lambda \exp(iE\lambda) \iiint_{-\infty}^{\infty} d^3 \boldsymbol{\mu} \\ & \times \int_{-\infty - i\Delta}^{\infty - i\Delta} d\alpha \alpha^{-1} \exp(i\varepsilon\alpha) \left[\prod_{i=1}^3 I(p_{xi}) I(p_{yi}) I(p_{zi}) \right] I(p_{\theta 1}) I(p_{\phi 1}). \end{aligned}$$

The momentum integrations are all of the type

$$\int_{-\infty}^{\infty} dx \exp(-iax^2 + ibx) = \text{const.} a^{-1/2} \exp(ib^2/4a),$$

and we have

$$I(p_{xi}) = \int_{-\infty}^{\infty} dp_{xi} \exp(-i\lambda p_{xi}^2/2m_i + i\mu_x p_{xi}) = \text{const.} \lambda^{-1/2} \exp(im_i \mu_x^2/2\lambda).$$

Similarly we have

$$I(p_{yi}) = \text{const.} \lambda^{-1/2} \exp(im_i \mu_y^2/2\lambda),$$

$$I(p_{zi}) = \text{const.} \lambda^{-1/2} \exp(im_i \mu_z^2/2\lambda),$$

$$I(p_{\theta 1}) = \text{const.} (\lambda + \alpha)^{-1/2},$$

and

$$I(p_{\phi 1}) = \text{const.} (\lambda + \alpha)^{-1/2} \sin \theta_1.$$

After integration over μ , we have

$$\mathcal{V}(\varepsilon) = \text{const.} \int_{-\infty}^{\infty} d\lambda \lambda^{-3} \exp(iE\lambda) \int_{-\infty-i\lambda}^{\infty-i\lambda} d\alpha \alpha^{-1} (\alpha + \lambda)^{-1} \exp(i\varepsilon\alpha),$$

where the integral with respect to the spatial coordinates and angles is independent of ε and therefore put into the constant. Integration over α can be done by the method of residues, and we have

$$\mathcal{V}(\varepsilon) = \text{const.} [E^3 - (E - \varepsilon)^3],$$

or

$$\frac{d\mathcal{V}(\varepsilon)}{d\varepsilon} = \text{const.} (E - \varepsilon)^2 d\varepsilon.$$

By substituting $BK(K+1)$ and $B(2K+1)$ for ε and $d\varepsilon$, respectively, we have

$$N(K) = \text{const.} (2K+1)[E - BK(K+1)]^2,$$

for the number of CH^* radicals in the rotational state with the quantum number K . Then the intensity of a rotational line is written as

$$I_K = CP_K N(K),$$

where C is nearly constant and $(2K+1)P_K$ is the intensity factor whose theoretical expres-

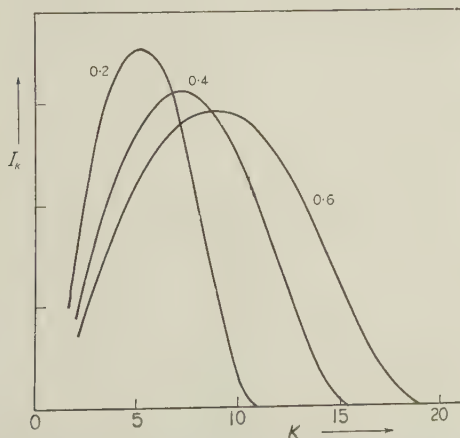


Fig. 4. The theoretical distribution of rotational intensity I_K against rotational quantum number K . The numeral attached to each curve means the excess potential energy E in eV.

sion has already been presented elsewhere¹⁰⁾.

In Fig. 4, I_K is plotted against K in cases of several different values of E . As compared with Fig. 1, Fig. 4 tells us that the value of E for C_2H_2 may be estimated as 0.4 eV. The same argument as above may be valid also when the parent molecule CH_2O splits into pieces as is seen from Fig. 2, that is



One of the authors wishes to express his sincere thanks to Professor K. Husimi for his kind advice in regard to the theoretical interpretation of the experimental results. This work was supported in part by the Scientific Research Fund of the Ministry of Education.

References

- 1) T. Horie, T. Nagura and M. Otsuka: Phys. Rev. **104** (1956) 547.
- 2) T. Horie, T. Nagura and M. Otsuka: J. Phys. Soc. Japan **11** (1956) 1157.
- 3) T. Horie, T. Nagura and M. Otsuka: Ann. Rep. Scient. Works, Fac. Sci. Osaka Univ. **4** (1956) 11.
- 4) T. Horie, T. Nagura and M. Otsuka: J. Phys. Soc. Japan **12** (1957) 500.
- 5) T. Horie, M. Otsuka and T. Nagura: J. Phys. Soc. Japan **12** (1957) 1099.
- 6) T. Horie, S. Watanabe and K. Kurata: J. Chem. Phys. **31** (1959) 783.
- 7) A. Langer: J. Phys. and Coll. Chem. **54** (1950) 618.
- 8) G. Herzberg: *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951) II, 288, 302.
- 9) W. C. Price: Phys. Rev. **47** (1935) 444.
- 10) W. Jevons: *Report on Band-Spectra of Diatomic Molecules* (The Physical Society, London, 1932) 136.
- 11) R. H. Milburn: Revs. Mod. Phys. **27** (1955) 1.

Microwave Spectrum of *cis*-1,2-Dichloroethylene

By Tadao SHIMIZU and Hiroshi TAKUMA*

*Department of Physics, Faculty of Science,
University of Tokyo, Tokyo, Japan*

(Received November 13, 1959)

The microwave spectrum of *cis*-1,2-dichloroethylene was observed in the frequency range between 20 and 25 kMc/sec. The determined molecular parameters, $d_{\text{CCl}}=1.724$ Å and $\angle\text{CCCl}=121^\circ33'$ on the assumption of $d_{\text{CC}}=1.32$ Å, $d_{\text{CH}}=1.07$ Å and $\angle\text{CCH}=120^\circ$, show good agreements with the parameters of vinylidene chloride, which was studied previously in this laboratory. The quadrupole hyperfine coupling constants were found to be $eQq_{aa}=2$ Mc/sec, $eQq_{bb}=-22$ Mc/sec and $eQq_{cc}=20$ Mc/sec.

§ 1. Introduction

The carbon chlorine bond length in molecules has been studied by some authors^{1), 2)} in relation to the bond characters and the electronic structures around the bonding atoms. A number of chlorine substituted ethylene molecules have been examined by electron diffraction method and infrared and microwave spectroscopy. The results are listed in Table I. The bond lengths have been obtained on some assumptions of molecular parameters, in most cases d_{CC} , d_{CH} and $\angle\text{CCH}$, for lack of independent data to deter-

mine the molecular geometry. Assumed C-C distances are grouped into two sets, one is about 1.38 Å and the other about 1.32 Å. Consequently the calculated C-Cl distance is about 1.72 Å in the latter case and about 1.67 Å in the former case. By measuring and analyzing the rotational spectrum of *cis*-1,2-dichloroethylene, $\text{CHCl}=\text{CHCl}$, the determination of the most plausible values of d_{CCl} and d_{CC} and other structural constants of this molecule was tried. The quadrupole hyperfine structure and its relation to C-Cl bond were also discussed.

Table I. C-C and C-Cl bond lengths of various chlorine substituted ethylene molecules.

Molecule	d_{CC}	d_{CCl}	Method	Ref. and date
$\text{CHCl}-\text{CHCl}$	1.38 Å (assumed)	1.67 Å	e.d.	(7) 1935
$\text{CClCl}-\text{CClCl}$	1.38 Å (assumed)	1.73 Å	e.d.	(7) 1935
$\text{CClCl}-\text{CHH}$	1.38 Å (assumed)	1.69 Å	e.d.	(4) and (7) 1935
$\text{CClCl}-\text{CClCl}$	1.30 Å	1.72 Å	e.d.	(5) 1952
$\text{CHCl}-\text{CHH}$	1.38 Å (assumed)	1.69 Å	m.s.	(6) 1956
$\text{CClCl}-\text{CHH}$	1.32 Å (assumed)	1.72 ₇ Å	m.s.	(1) 1957

e.d.: electron diffraction

m.s.: microwave spectroscopy

§ 2. Experiment

The structure of *cis*-1,2-dichloroethylene molecule is planar with a two-fold symmetry axis. The principal axes of this molecule are shown in Fig. 1. The structure of this molecule was already determined by Brockway⁷⁾ by electron diffraction method as $d_{\text{CCl}}=1.67$ Å, $d_{\text{CC}}=1.38$ Å (assumed) and $\angle\text{CCCl}=123^\circ30'$. The permanent dipole moment of the most abundant isotopic species lies along

* Present address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Tokyo, Japan.

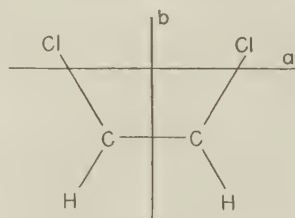


Fig. 1.

the *b*-axis, thus only *b*-type transitions are detectable. The sample is the colorless liquid and boils at 60°C . Some of the lines were observed at dry-ice temperature with higher

resolution. Because it is a strong solvent, greaseless stopcocks and joints made of metal were used and the Stark electrode was supported by teflon plates. The sample, containing 60% *cis*-1,2-dichloroethylene, was obtained from the Asahi Dow Chemical Company by courtesy of Dr. Y. Tsunoda. The commercially available sample was also used to discriminate the absorption lines due to impurity molecules. An ordinary Stark modulation spectrometer with sine-wave modulation at 100 kc/sec superposed on a *dc* voltage was used. Square-wave modulation at 6 kc/sec was also used in order to observe the hyperfine structure in higher resolution. The absorption cell was three meters long with teflon seals. A klystron 2K33 and a crystal tripler driven by a klystron 2K26 were used as the microwave source. About eighty lines were measured in the frequency range between 20 and 25 kMc/sec. Fifteen lines were assigned, while unassigned lines were considered as transitions of larger *J* values, lines of vibrationally excited states or lines due to impurity molecules. The assigned lines are listed in Table II. The quadrupole hyperfine structure of this molecule was so complicated that each line was observed as a broad line with unresolved hyperfine structure. Thus we could not assign the *J* values of rotational states from their Stark behaviors. Some of

$$J=4 \quad \Delta J=\Delta F=0$$



$$J=11 \quad \Delta J=\Delta F=0$$



Fig. 2. Calculated patterns of quadrupole hyperfine transitions.

Table II. Assigned lines.

Obs. Freq. (Mc/sec)	Int.	Assignment	Calc. Freq. (Mc/sec)	Note
21161.6	MW	8 ₁₇ ←8 ₀₈ *	21161.7	multiplet
21399.2	WW	6 ₂₄ ←6 ₁₅	21399.0	
21485.3	MS	9 ₂₇ ←9 ₁₈	21482.0	
21772.3	WW	8 ₁₇ ←7 ₂₆ *	21771.5	
21916.2	MS	8 ₁₇ ←8 ₀₈	21920.2	
22049.0	W	5 ₂₃ ←5 ₁₄	22047.2	doublet
22181.0				
22183.1	MW	10 ₂₈ ←10 ₁₉ *	22183.8	doublet
22501.8	MS	11 ₂₉ ←11 ₃₈	22501.4	
22507.3	MS	10 ₂₈ ←10 ₁₉	22504.3	
22833.4	M	4 ₂₂ ←4 ₁₃	22834.4	
22869.4				
22873.9	MS	6 ₀₆ ←5 ₁₅ *	22870.5	triplet
23236.9	MS	8 ₁₇ ←7 ₂₆	23237.5	triplet
23620.5	W	11 ₂₉ ←11 _{1,10} *	23619.5	triplet
24137.0	W			
24140.1	M	11 ₂₉ ←11 _{1,10}	24141.5	triplet
24143.2	W			
24943.3	WW	9 ₁₈ ←9 ₀₉	24943.5	

* lines of CHCl₃³⁶=CHCl₃³⁷

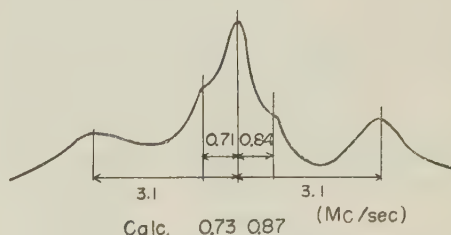


Fig. 3. Observed (zero-field) line shape of 11₂₉←11_{1,10} line.

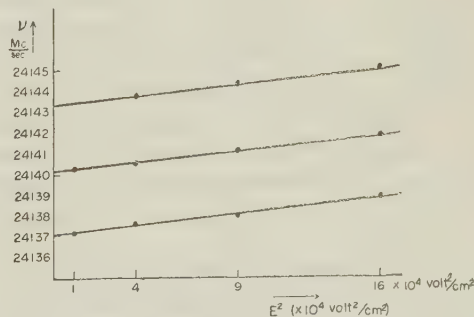


Fig. 4. Observed Stark behavior of 11₂₉←11_{1,10} line, showing quadrupole triplet.

the lines were observed as triplets, which are expected from the calculation of the weighted means of hyperfine components as shown in Fig. 2. Observed line shape of *J*=11₂₉←11_{1,10} transition is shown in Fig. 3. The accuracy of frequency measurement was essentially limited by the broad line width,

and the errors in measured frequencies were estimated as ± 0.5 Mc/sec for the stronger lines and ± 1 Mc/sec for the weaker lines.

§ 3. Analysis

For the assignment of the spectral lines, we adopted the method of κ vs $(A-C)/2$ diagram⁸⁾. The values of $(A-C)/2$ and κ were determined from several strong lines which belong to Q -branch transitions. Using a relation $1/C=1/A+1/B$, we obtained the approximate values of A , B and C , which are sufficiently accurate to assign R -branch transitions. From all of the assigned lines rotational constants and asymmetry parameter were recalculated. Using the calculated structural parameters of $\text{CHCl}^{35}=\text{CHCl}^{35}$ molecule, we assigned the lines of the isotopic molecule $\text{CHCl}^{35}=\text{CHCl}^{37}$. The rotational constants of the isotopic molecule were calculated from the observed frequencies and are listed in Table III, as well as the values of its

Table III. Rotational constants and moments of inertia of cis-1,2-dichloroethylene.

	$\text{CHCl}^{35}-\text{CHCl}^{35}$	$\text{CHCl}^{35}-\text{CHCl}^{37}$
$(A+C)/2$ (Mc/sec)	6521.4	6455.1
$(A-C)/2$ (Mc/sec)	4329.3	4319.6
κ	-0.87197	-0.87782
A (Mc/sec)	10850.8	10774.7
B (Mc/sec)	2746.4	2663.3
C (Mc/sec)	2192.1	2135.5
I_a (amuA ²)	46.59	46.92 46.87*
I_b (amuA ²)	184.07	189.82 189.08*
I_c (amuA ²)	230.62	236.73 235.95*
d (amuA ²)	0.05	0.01

$$d = I_c - (I_a + I_b)$$

* moments of inertia of $\text{CHCl}^{35}=\text{CHCl}^{37}$ calculated from the structural parameters of $\text{CHCl}^{35}=\text{CHCl}^{35}$.

moments of inertia. The uncertainties of the moments of inertia due to the errors of ± 0.5 Mc/sec in the observed frequencies are ± 0.002 amu A² for I_a and ± 0.02 amu A² for I_b and I_c . The quantum defect is also of the same order of magnitude. The structural parameters were calculated within the accuracy of 10^{-4} . The error due to the uncertainties of assumed constants must appear in addition. Two parameters were determined assuming the values of three parameters as shown in Table IV.

Table IV. Structural parameters of $\text{CHCl}^{35}-\text{CHCl}^{35}$.

assumed values	d_{CC} 1.32 A	d_{CH} 1.07 A	$\angle \text{CCH}$ 120°
calculated values	d_{CCl} 1.72 ₄ A	$\angle \text{CCCl}$ 121°33'	

§ 4. Discussion

Because hydrogen is a light atom, the assumptions of the values of d_{CH} and $\angle \text{CCH}$ do not appreciably affect the calculation of d_{CCl} . The assumption of the value of d_{CC} , however, gives an influence on the value of d_{CCl} to some extent. The values of d_{CC} and d_{CCl} obtained by electron diffraction method and infrared⁴⁾ and microwave spectroscopy, have given considerably different values. Pauling³⁾ assumed the value of d_{CC} as 1.38 A in electron diffraction study on tetrachloroethylene. On the other hand, Karle and Karle⁵⁾ obtained the value as 1.30 A for the same molecule. Recently, the value of d_{CC} have been determined for ethylene as follows: Coulson⁹⁾ obtained the value of 1.34 A from the Raman spectra of ethylene and deuterioethylene molecules; Allen and Plyler¹⁰⁾ obtained 1.337 A from infrared spectrum; Bartell and Bonham¹¹⁾ obtained 1.334 A by electron diffraction. In the case of chlorine substituted ethylenes as 1,2-dichloroethylene, vinylidene chloride and vinyl chloride, two parameters d_{CC} and d_{CCl} can not be determined independently. If we take the value of d_{CC} as 1.32 ~ 1.34 A, the values of d_{CCl} for those chlorine

Table V. Assumed values of d_{CC} and calculated values of d_{CCl} in various chlorine substituted ethylene molecules.

d_{CC} (assumed)	1.38 A	1.34 A	1.32 A	1.30 A
$\text{CHCl}-\text{CHCl}$	1.706 A	1.711 A	1.724 A	1.729 A
$\text{CClCl}-\text{CHH}$	1.67 A		1.727 A	
$\text{CHCl}-\text{CHH}$	1.69 A	1.724 A		

substituted ethylenes are found to be approximately the same, in agreement with the discussion of Sekino and Nishikawa¹⁾ as shown in Table V.

Since the carbon atom in sp^2 hybridized state is more electronegative than in sp^3 , the ionic character of carbon chlorine bond

in sp^2 state is smaller than that in sp^3 state. The C-Cl bond in 1,2-dichloroethylene molecule, however, may be more ionic than that in 1,1-dichloroethylene molecule. Because in the former molecule each carbon atom is bound to only one chlorine atom, which is more electronegative, while in the latter, it is bound to two chlorine atoms. According to Pauling's formula¹²⁾ and Schomaker and Stevenson's formula¹³⁾, for the ordinary percentage of double bond character and rather large percentage of ionic character of the bond, the calculated C-Cl bond length is compared with the experimental result in Table VI. On the assumption of the larger value

Table VI. Calculated and experimental values of d_{CCl} in chlorine substituted ethylene molecules.

double bond character	ionic character	d_{CCl} (calc.)	d_{CCl} (exp.)
10%	15%	1.73 Å	1.71~1.72 Å
	20%	1.71 Å	

of d_{CC} , the value of d_{CCl} becomes so small that it requires unreasonably large amount of s -hybridization of chlorine atom.

§ 5. The Analysis of Quadrupole Hyperfine Structure

Since dichloroethylene molecule contains two nuclei with spin $3/2$, the quadrupole hyperfine structure of the molecule is complicated. The theory was already worked out by Robinson and Cornwell¹⁴⁾. According to their theory there appear more than sixteen hyperfine components in a few megacycles region. These components could not be resolved by the usual absorption type spectrometer. The calculated relative intensities of these components are shown in Fig. 2 for $J=11$ and $J=4$ of Q -branch lines. In the high J cases of Q -branch transitions, for example $11_{20} \leftarrow 11_{1,10}$ transition, the quadrupole hyperfine components are found in three groups and can be observed as a triplet. On the other hand in low J cases, as in $4_{22} \leftarrow 4_{13}$ transition, the hyperfine components are not grouped in such a way. Only the hyperfine structure of $11_{20} \leftarrow 11_{1,10}$ line was observed as a resolved triplet. Moreover, two weak satellites were observed in both sides of the center line as shown in Fig. 3 under high resolution

at dry-ice temperature. The Stark effects of these hyperfine components were measured.

The quadrupole coupling constants along the principal inertia axes were obtained as $eQq_{aa}=2$ Mc/sec, $eQq_{bb}=-22$ Mc/sec and $eQq_{cc}=20$ Mc/sec. These values are transformed into the direction of principal axes of q tensor. The bond direction may be somewhat different from one of the principal axes of the q tensor, because the electron cloud of each chlorine atom is attracted by two carbon atoms which are positively ionized. The principal axes of the q tensor x , y and z are so chosen that z axis is perpendicular to the molecular plane and the x axis lies nearest to the CCl bond. Assuming the angle between x axis and the C-C bond as 125° , we obtained the values of $eQq_{zz}=-46$ Mc/sec and $\eta=(eQq_{zz}-eQq_{yy})/eQq_{zz}=0.13$. On the other hand, the quadrupole coupling constants in molecules can be estimated assuming the appropriate ionic and double bond characters of the bond and s -characters of the bonding electron orbitals. The coupling constant eQq_{zz} with which the direct comparison of the experimental value of eQq_{cc} is possible without any assumption of the direction of the principal axis of q -tensor, is calculated from the value of eQq_{310} of the chlorine atom by the following formula,

$$eQq_{zz}=[1/2(1-s)(1-\alpha-\beta) - 1/2(1+s)(1+\varepsilon)\alpha]eQq_{310},$$

where s is the s -character of p_σ bonding orbital of the chlorine atom, α the double bond character of the bond, β the ionic character of the bond, and ε the correction factor due to the ionization of the chlorine atom¹⁵⁾. Assuming the usually adopted values, $s=0.15$, $\alpha=0.15$ and $\beta=0.15$, we get $eQq_{zz}=23.7$ Mc/sec. However, as the bond is more ionic than other types of molecules as stated above, rather large value of $\beta=0.2$ is adopted, and we obtain $eQq_{zz}=19.5$ Mc/sec and $eQq_{\text{bond}}=-48$ Mc/sec. These calculated values show a fairly good agreement with our experimental result.

Acknowledgement

The authors express their hearty thanks to Professor K. Shimoda for his continuous encouragement and kind guidance throughout this work. They also thank to Dr. T. Nishikawa for his valuable discussions, and Dr. Y. Tsunoda for supplying the sample.

References

- 1) S. Sekino and T. Nishikawa: J. Phys. Soc. Japan **12** (1957) 43.
- 2) J. Duchesne: J. Chem. Phys. **19** (1951) 246; Trans. Faraday Soc. **46** (1950) 187.
- 3) L. O. Brockway, J. Y. Beach and L. Pauling: J. Amer. Chem. Soc. **57** (1935) 2693. L. Pauling, L. O. Brockway and J. Y. Beach: J. Amer. Chem. Soc. **57** (1935) 2705.
- 4) W. S. Gallaway and E. F. Barker: J. Chem. Phys. **10** (1942) 88.
- 5) I. L. Karle and J. Karle: J. Chem. Phys. **20** (1952) 63.
- 6) J. H. Goldstein: J. Chem. Phys. **24** (1956) 106.
- 7) L. O. Brockway: Rev. Mod. Phys. **8** (1936) 231.
- 8) W. Gordy, W. V. Smith and R. F. Trambarulo: *Microwave Spectroscopy* (John Wiley and Sons, 1953).
- 9) private communication to Dr. Nishikawa.
- 10) H. C. Allen Jr. and E. K. Plyler: J. Amer. Chem. Soc. **80** (1958) 2673.
- 11) C. S. Bartell and R. A. Bonham: J. Chem. Phys. **27** (1957) 1414.
- 12) L. Pauling: *The Nature of Chemical Bond* (Cornell Univ. Press, Ithaca, New York, 1945) 175.
- 13) V. Schomaker and D. P. Stevenson: J. Amer. Chem. Soc. **63** (1941) 37.
- 14) G. W. Robinson and C. D. Cornwell: J. Chem. Phys. **21** (1953) 1436.
- 15) C. H. Townes and A. L. Schawlow: *Microwave Spectroscopy* (McGraw-Hill, 1955).

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

Theory of Solutions of Chain Molecules

By Hiroshi OKAMOTO

*The Electrical Communication Laboratory,
Nippon Telegraph and Telephone Public Corporation,
Kichijoji, Musashino, Tokyo, Japan*

(Received November 36, 1959)

Using the first order Bethe's approximation, a theory of solution of chain molecules is developed. Though it is a well-known fact that the first order Bethe's approximation and the method of the quasi-chemical equilibrium coincide with each other for the case of lattice gas or solutions of short chain, this coincidence is found to be not always true for solutions of long chain molecules. The obtained results have the favorable characteristics which the experimental facts require.

§1. Introduction

Many years have past since the pioneering work of Flory's¹⁾ quasi-crystalline model of chain polymer solution developed. Miller²⁾, Orr³⁾, Guggenheim⁴⁾ and other investigators⁸⁾ also studied the similar problem and succeeded to explain the general features of chain polymer solutions.

In spite of the general success of these theories, there are many departures from the experimental results in detailed points. For example, these are the problems of the complicated concentration dependency of the mixing energy⁵⁾ or that the experimental values of the concentration at the critical mixing

point give almost twice larger values⁶⁾ than those the theories predict. The concentration dependencies of the interaction parameter⁷⁾ or else⁸⁾ were somewhat artificially assumed to explain these problems. But such methods seem to be undesirable.

In the following, we will discuss such problems from the point of view considering the detail configurations of the polymer chains and show the obtained results have the favorable characteristics which the experimental facts require. Though it is a well-known fact that the first order Bethe's approximation and the quasi-chemical equilibrium coincide with each other in the case of lattice gas or that of the

solution of short chain molecules. This coincidence is found to be not always true for long chain molecules.

§ 2. The First Order Bethe's Approximation

We consider a lattice space of which coordination number is z . The system consists of n_α , α type chain molecules and n_β , β type solvent molecules. The α type chain molecule consists of n elements which occupy n continuous lattice sites, the β type solvent molecule is a point molecule occupying one site. The first neighbour pairs of two elements ($\alpha \sim \alpha$), ($\beta \sim \beta$) and ($\alpha \sim \beta$) contribute the potential energies of $\varepsilon_{\alpha\alpha}$, $\varepsilon_{\beta\beta}$ and $\varepsilon_{\alpha\beta}$ respectively.

The first order Bethe's approximation considers in detail all the possible configurations

that can be illustrated on a set of $z+1$ sites consisting of a central one and its first coordination shell, provided that the first shell sites are not themselves closest neighbours. These $z+1$ sites is called as local system hereafter. The outer part of the local system affects the detailed configurations on the local system in the following way. (Fig. 1)

When a chain takes a configuration in which three consecutive elements of the chain occupy the central site and the two of the first shell sites, whereas the other elements of the chain never assume the first shell sites, the outer part weights the configuration by a factor $\lambda_{\alpha,1}$.

When the chain takes a configuration in which it passes through the central site and one element of the same chain (other than the two elements consecutive to the one on the central site) occupies one of the first shell sites, the weight is $\lambda_{\alpha,2}$.

When the chain takes a configuration in which the chain passes through the central and also occupies $l-1$ sites out of the $z-2$ first shell sites, the weight is $\lambda_{\alpha,l}$, and particularly if the end elements of the chain occupy the central site in the above case, the weight is $\varepsilon_l \lambda_{\alpha,l}$.

When the chain occupies one or two of the first shell sites, (never assuming the central site) the weights are $\varepsilon \lambda_\alpha$ and $\delta \lambda_\alpha^2$ respectively.

For simplicity, we do not consider the configurations in which more than three of the first shell sites are occupied (the central is not).

When a solvent molecule occupies any one of the $z+1$ sites, the weight is λ_β .

Two functions A and B are defined by

$$A = \varepsilon \lambda_\alpha x_{\alpha\alpha} + \lambda_\beta x_{\alpha\beta},$$

$$B = \varepsilon \lambda_\alpha x_{\alpha\beta} + \lambda_\beta x_{\beta\beta},$$

where,

$$x_{\alpha\alpha} = \exp[-\varepsilon_{\alpha\alpha}/kT], \quad x_{\beta\beta} = \exp[-\varepsilon_{\beta\beta}/kT],$$

$$x_{\alpha\beta} = \exp[-\varepsilon_{\alpha\beta}/kT].$$

The local partition function G is written as follows.

$$G = \sum_l G_{\alpha,l} + G_\beta, \quad (2.1)$$

where,

$$G_{\alpha,l} = \binom{z}{2} \lambda_{\alpha,l} \sum_r \left(\binom{z-l-1}{r} \right) (\delta \lambda_\alpha^2 x_{\alpha\alpha}^2)^r A^{z-l-1-2r} + z \varepsilon_l \lambda_{\alpha,l} \sum_r \left(\binom{z-l}{r} \right) (\delta \lambda_\alpha^2 x_{\alpha\alpha}^2)^r A^{z-l-2r}, \quad (2.2)$$

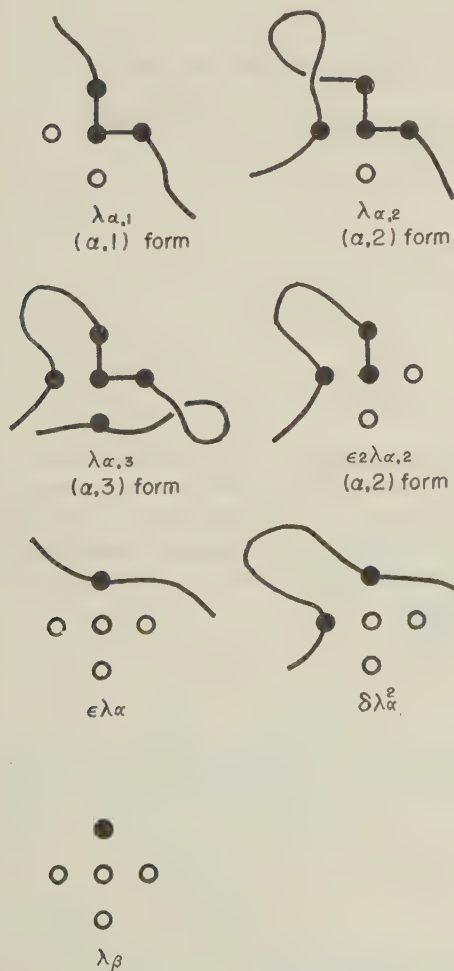


Fig. 1. The various forms of a chain and a point (solvent) molecules on the $z+1$ sites (the local system) and their weight factors.

$$G_{\alpha, z-1} = \binom{z}{2} \lambda_{\alpha, z-1} + \varepsilon_{z-1} \lambda_{\alpha, z-1} A + z \varepsilon_z \lambda_{\alpha, z}, \quad (2.3)$$

$$G_{\beta} = \lambda_{\beta} \sum_r \left(\binom{z}{r} \right) (\delta \lambda_{\alpha}^2 x_{\alpha\alpha}^2)^r B^{z-2r}. \quad (2.4)$$

The symbol such as $\left(\binom{z-l-1}{r} \right)$ means the number of ways to select any r site pairs from $z-l-1$ sites.

(I) If we assume that

$$\lambda_{\alpha, l} = 0 \quad l \geq 2 \\ \delta = 0,$$

this is the case that a chain never passes through the local system more than once.

Orr's work³⁾ corresponds to this case. According to his results, the average number of ($\alpha \sim \beta$) contacts, $z\bar{X}$ is given by

$$z\bar{X} = \frac{z q_{\alpha} n_{\alpha} n_{\beta}}{q_{\alpha} n_{\alpha} + n_{\beta}} \cdot \frac{2}{1 + \beta}, \quad (2.5)$$

$$z q_{\alpha} = n z - 2n + 2, \quad (2.6)$$

$$\beta^2 = 1 + 4\xi(1 - \xi) \left(\exp \left[\frac{2w}{kT} \right] - 1 \right), \quad (2.7)$$

$$\xi = \frac{q_{\alpha} n_{\alpha}}{q_{\alpha} n_{\alpha} + n_{\beta}}, \quad (2.8)$$

$$2w = 2\varepsilon_{\alpha\beta} - (\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta}). \quad (2.9)$$

This is the well-known case that first order Bethe's approximation leads the same formula for $\bar{X}$ as that given by the quasi-chemical equilibrium.

(II) Next we assume that

$$\lambda_{\alpha, l} \neq 0 \quad l \geq 1 \\ \delta = 0.$$

The procedure of the first order Bethe's approximation is to make the probability of the occupation of the central site and a first shell site by an α and β molecule respectively equal to the probability of occupation in the reverse manner. This equivalence is expressed in a formal way by the relation

$$\lambda_{\alpha} \frac{\partial G_{\beta}}{\partial \lambda_{\alpha}} = \lambda_{\beta} \sum_l \frac{\partial G_{\alpha, l}}{\partial \lambda_{\beta}}. \quad (2.10)$$

We consider that in the equilibrium state, the relative probability of the occurrence of the configuration that an α molecule takes an (α, l) form is described by $p(l)$,

$$G_{\alpha, l} / G_{\alpha, 1} = p(l). \quad (2.11)$$

The probability function $p(l)$ depends on the state of the whole system such as the concentration, the temperature and may be considered to have a close relation with the equilibrium extension of the chain molecule.

Further, the ratio of the probability of the occupation of the central site by the end elements to that of the other elements is represented by $q(l)$, given by

$$\frac{z \varepsilon_l \lambda_{\alpha, l} A^{z-l}}{\left(\binom{z}{2} \lambda_{\alpha, l} A^{z-l-1} \right)}. \quad (2.12)$$

After applying Eqs. (2.2), (2.3) and (2.4) to Eq. (2.10), we use the relations (2.11) and (2.12). Then,

$$z \varepsilon \lambda_{\alpha} \lambda_{\beta} x_{\alpha\beta} B^{z-1} \\ = \left(\binom{z}{2} \lambda_{\alpha, 1} \lambda_{\beta} x_{\alpha\beta} A^{z-3} \sum_l \frac{1 + q(l)}{1 + q(l)} p(l) \{z-l-1\} \right. \\ \left. + (z-l)q(l) \right). \quad (2.13)$$

The equilibrium properties of the whole system are also given by

$$\frac{v_{\alpha}}{v_{\beta}} = \frac{\sum G_{\alpha, l}}{G_{\beta}}, \quad (2.14)$$

where v_{α} and v_{β} are the volume concentrations of α and β molecules respectively.

We use the the abbreviation that

$$q_{\alpha}' = \frac{\sum_l \frac{p(l)}{1 + q(l)} \{z-l-1\} + (z-l)q(l)}{\frac{z}{n} \sum_l p(l)} \quad \left. \begin{aligned} &= \frac{n z - 2n + 2 - \rho}{z}, \\ &\rho = \sum_l (l-1) \sum_j Q_{jl}, \\ &q(l) = \frac{2Q_{1l}}{\sum_{j=2}^{n-1} Q_{jl}}. \end{aligned} \right\} \quad (2.15)$$

Where Q_{jl} is the probability that when the j th element of a chain passes through the central site, $l-1$ elements of the same chain, other than the two elements consecutive to the one on the central, also occupy the first shell sites.

$\bar{X}$ must equal to

$$\frac{\bar{X}}{n n_{\alpha} + n_{\beta}} = \frac{\partial G / \partial x_{\alpha\beta}}{2zG}. \quad (2.16)$$

Eqs. (2.13) (2.14) (2.15) and (2.16) give

$$\bar{X} = \frac{q_{\alpha}' n_{\alpha} n_{\beta}}{q_{\alpha}' n_{\alpha} + n_{\beta}} \cdot \frac{2}{1 + \beta'}, \quad (2.17)$$

$$\beta'^2 = 1 + 4\xi'(1 - \xi') \left(\exp \left[\frac{2w}{kT} \right] - 1 \right), \quad (2.18)$$

$$\xi' = \frac{q_{\alpha}' n_{\alpha}}{q_{\alpha}' n_{\alpha} + n_{\beta}}. \quad (2.19)$$

of the chain molecule. So, it is seen from $z q_{\alpha}'$ may be considered to be the effective number of possible contacting first neighbours

Eq. (2.17) that in the case II, the first order Bethe's method and the quasi-chemical equilibrium are equivalent in some senses. But it is important that q_{α}' should be determined so as to minimize the free energy of the whole system and q_{α}' is never constant but depends on the concentration or the temperature of the system.

(III) The most general case is

$$\lambda_{\alpha,l} \neq 0 \quad l \geq 1 \\ \delta \neq 0.$$

The relations (2.10), (2.11), (2.14) and (2.16) should also hold in this case but instead of Eq. (2.12) we must use the following,

$$\frac{z \varepsilon_l \lambda_{\alpha,l} \sum \left(\binom{z-l}{r} \right) (\delta \lambda_{\alpha}^2 x_{\alpha\alpha}^2)^r A^{z-l-2r}}{\binom{z}{2} \lambda_{\alpha,l} \sum \left(\binom{z-l}{r} \right) (\delta \lambda_{\alpha}^2 x_{\alpha\alpha}^2)^r A^{z-l-1-2r}} = q(l). \quad (2.12')$$

$$\left. \begin{aligned} \bar{X} &= \bar{X}' + \bar{X}'' , \\ \bar{X}' &= \frac{\{q_{\alpha}'' n_{\alpha} - (2r_{\beta}/z) n_{\beta}\} n_{\beta}}{q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta}} \cdot \frac{2}{1 - \frac{4r_{\beta} n_{\beta}/z}{q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta}} + \sqrt{1 + \frac{4q_{\alpha}'' n_{\alpha} n_{\beta}}{(q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta})^2} (e^{2w/kT} - 1)}} , \\ \bar{X}'' &= \frac{(2r_{\beta}/z) n_{\beta}^2 e^{2w/kT}}{q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta}} \cdot \frac{2}{1 + \frac{2}{q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta}} (e^{2w/kT} - 1) + \sqrt{1 + \frac{4q_{\alpha}'' n_{\alpha} n_{\beta}}{(q_{\alpha}'' n_{\alpha} + q_{\beta}' n_{\beta})^2} (e^{2w/kT} - 1)}} , \\ q_{\alpha}'' &= q_{\alpha}' - \frac{2r_{\alpha}}{z} , \quad q_{\beta}' = 1 - \frac{2r_{\beta}}{z} e^{2w/kT} , \end{aligned} \right\} \quad (2.21)$$

where r_{α} and r_{β} mean the number of chains which occupy two of the first shell sites when α or β molecule occupies the central site respectively,

$$r_{\alpha} = \frac{1}{\sum_l p(l)} \sum_l r_{\alpha,l} p(l) , \\ r_{\alpha,l} = \frac{\sum_r \binom{z}{r} \lambda_{\alpha,l} \left(\binom{z-l-1}{r} \right) r (\delta \lambda_{\alpha}^2 x_{\alpha\alpha}^2)^r A^{z-l-1-2r}}{G_{\alpha,l}} , \\ r_{\beta} = \frac{\sum_r \lambda_{\beta} \left(\binom{z}{r} \right) r (\delta \lambda_{\alpha}^2 x_{\alpha\alpha}^2)^r B^{z-2r}}{G_{\beta}} ,$$

To obtain r_{α} and r_{β} , we must make use of the relation (2.20). Unfortunately, this procedure is very complicated and it seems to be difficult to obtain the results in a closed form.

For example, for two dimensional hexagonal lattice, if the chain is sufficiently long so that,

$$\frac{1}{n} \ll 1 .$$

we obtain

$$r_{\alpha} = 0 \\ r_{\beta} = \frac{1-\rho/n}{R+2} v_{\alpha} + \frac{1-\rho/n}{R+2} v_{\alpha}^2 + \dots .$$

In addition to these relations, the next is necessary.

$$\varepsilon \frac{\partial G}{\partial \varepsilon} = R \delta \frac{\partial G}{\partial \delta} . \quad (2.20)$$

This relation means that a proportionality exists between the number of the chains which occupy one first shell site only and that of the chains which occupying two first shell sites only. Obviously R has a close relation with the equilibrium dimension of the chain, if the chain is more spreaded, R becomes larger and if the chain is more contracted, R becomes smaller. R , as well as ρ , should be determined so as to minimize the free energy of the whole system.

Making use of the Eqs. (2.10) (2.11) (2.12') and (2.14), Eq. (2.16) gives the expression for $\bar{X}$ as

We will not consider the problem further in this case, but it is noteworthy that in the case **III** the equivalence of the first order Bethe's approximation and the quasi-chemical equilibrium is no longer correct.

In the following we confine ourselves in the case **II**, because the formulas obtained in this case are relatively simple and yet seem to retain the characteristics we intend.

§ 3. The Thermodynamical Quantities

The partition function of the whole system, Ω , is written as follows.

$$\Omega = \sum_{\rho} \Omega(\rho). \quad (3.1)$$

$\Omega(\rho)$, which is the partition function of fixed ρ , can be written as usual.

$$\Omega(\rho) = \Omega_0 \exp \left[\frac{-z \bar{X} w}{kT} \right] \sum w(n_{\alpha}, n_{\beta}, \rho, X), \quad (3.2)$$

$$\Omega_0 = \zeta_{\alpha}^{n_{\alpha}} \zeta_{\beta}^{n_{\beta}} \exp \left[\frac{-1}{kT} \left\{ \frac{z}{2} q_{\alpha} n_{\alpha} \epsilon_{\alpha\alpha} + \frac{z}{2} n_{\beta} \epsilon_{\beta\beta} \right\} \right], \quad (3.3)$$

$$\bar{X} = T \int_0^{1/T} \bar{X}(\rho) d\left(\frac{1}{T}\right), \quad (3.4)$$

where, ζ_{α} and ζ_{β} are the kinetic energy terms and $\sum_X \omega(X)$ is the number of configurations under constant ρ . $\bar{X}(\rho)$ is the statistical mean of X for the constant ρ ,

$$z \bar{X}(\rho) = -kT \frac{\partial \log \Omega(\rho)}{\partial w}.$$

We can generally follow the Orr's method to derive the terms $\bar{X}$ and $\sum_X \omega(X)$. Orr had used $z(z-1)^{n-2}$ for the number of configurations of the isolated chain. This factor is replaced by $f(\rho)$ in our case. $f(\rho)$ is the total number of configurations which the isolated chain of constant ρ takes.

The free energy of the whole system $F = -kT \log \Omega$ can be well approximated by the maximum $\Omega(\rho)$ in Eq. (3.1),

$$F = -kT \log \Omega(\rho).$$

The following formula of F is the formal extension of the Orr's formula in our case.

$$\begin{aligned} F = F_0 + \frac{zkT}{2} & \left\{ q_{\alpha'} n_{\alpha} \log \frac{\beta' - 1 + 2\xi'}{\xi'(\beta' + 1)} + n_{\beta} \log \frac{\beta' + 1 - 2\xi'}{(1 - \xi')(\beta' + 1)} \right\} \\ & + \frac{N}{n} kT \left\{ \frac{n(n-1)}{n - q_{\alpha'}} \log \frac{n}{n - q_{\alpha'}} + v_{\alpha} \log \frac{2}{f(\rho)z(z-1)} \frac{1}{n} \left(\frac{n}{n - q_{\alpha'}} \right)^{n-1} \right. \\ & \left. - (n-1) \left(\frac{n}{n - q_{\alpha'}} - v_{\alpha} \right) \log \left(\frac{n}{n - q_{\alpha'}} \right) + v_{\alpha} \log v_{\alpha} + n(1 - v_{\alpha}) \log (1 - v_{\alpha}) \right\}. \end{aligned} \quad (3.5)$$

F must satisfy the relation,

$$\frac{\partial F}{\partial \rho} = 0,$$

or

$$\begin{aligned} & -\frac{kT}{2} n_{\alpha} \log \frac{\beta' - 1 + 2\xi'}{\xi'(\beta' + 1)} + \frac{N}{n} kT \left[-\frac{n-1}{nz} \left(\frac{n}{n - q_{\alpha'}} \right)^2 \log \frac{n}{n - q_{\alpha'}} + v_{\alpha} \left\{ -\frac{d}{d\rho} \log f \frac{n-1}{z(n - q_{\alpha'})} \right\} \right. \\ & \left. + \frac{n-1}{nz} \left(\frac{n}{n - q_{\alpha'}} \right)^2 \log \left(\frac{n}{n - q_{\alpha'}} - v_{\alpha} \right) \right] = 0. \end{aligned} \quad (3.6)$$

ρ is determined from the above equation.

The mixing energy ΔH is

$$\Delta H = \frac{zq_{\alpha'}n_{\alpha}n_{\beta}}{q_{\alpha'}n_{\alpha}+n_{\beta}} \cdot \frac{2w}{1+\beta} \quad (3.7)$$

The mixing entropy ΔS is derived from

$$T\Delta S = \Delta H - \Delta F \quad (3.8)$$

The chemical potentials of α and β components are

$$\mu_{\alpha} = \left(\frac{\partial F}{\partial n_{\alpha}} \right)_{\rho, n_{\beta}} + \left(\frac{\partial F}{\partial \rho} \right) \frac{\partial \rho}{\partial n_{\alpha}} = \left(\frac{\partial F}{\partial \rho} \right)_{\rho, n_{\alpha}},$$

$$\begin{aligned} \frac{1}{kT} \mu_{\alpha} = & -\zeta_{\alpha} + \frac{zq_{\alpha}}{2kT} \epsilon_{\alpha\alpha} + \frac{z}{2} q_{\alpha'} \log \frac{\beta' - 1 + 2\xi'}{\xi'(\beta' + 1)} - \log \left(\frac{z}{2} \right) n f + \frac{(n-1)q_{\alpha'}}{n-q_{\alpha'}} \log \frac{n}{n-q_{\alpha'}} \\ & - \frac{(n-1)q_{\alpha'}}{n-q_{\alpha'}} \log \left(\frac{n}{n-q_{\alpha'}} - v_{\alpha} \right) + \log v_{\alpha}, \end{aligned} \quad (3.9)$$

$$\begin{aligned} \frac{1}{kT} \mu_{\beta} = & -\zeta_{\beta} + \frac{z}{2kT} \epsilon_{\beta\beta} + \frac{z}{2} \log \frac{\beta' + 1 - 2\xi'}{(1-\xi')(\beta' + 1)} - \frac{n-1}{n-q_{\alpha'}} \log \left(1 - \frac{n-q_{\alpha'}}{n} v_{\alpha} \right) \\ & + \log (1 - v_{\alpha}). \end{aligned} \quad (3.10)$$

The critical mixing point is determined by the following simultaneous equations.

$$\begin{aligned} \frac{\partial \mu_{\alpha}}{\partial v_{\alpha}} &= 0, \\ \frac{\partial^2 \mu_{\alpha}}{\partial v_{\alpha}^2} &= 0. \end{aligned}$$

The results are very complicated but if the chain is sufficiently long, it is found that the critical concentration is proportional to $1/\sqrt{n}$ and $\rho(v)$ may be well approximated in its expanded form in v_{α} .

$$\rho(v_{\alpha}) = \rho_0 + \rho_1 v_{\alpha}.$$

The approximate solutions of the critical point are

$$v_{\alpha, c} = \frac{1}{\sqrt{n}} \sqrt{\frac{z^2}{\{z-2-(\rho_0/n)\}\{z-1-2(\rho_0/n)\}+1.5(\rho_1/nz)}}, \quad (3.11)$$

$$\exp \left[\frac{2w}{kT_c} \right] = 1 + \frac{1}{z-2-(\rho_0/n)} + \frac{2}{\sqrt{n}} \frac{1.5z\rho_1}{(z-2-(\rho_0/n)) \sqrt{\frac{z-1-2(\rho_0/n)}{z-2-(\rho_0/n)} + \frac{1.5z\rho_1}{\{z-2-(\rho_0/n)\}^2 n}}}. \quad (3.12)$$

§ 4. The Derivation of $f(\rho)$

We now consider that the partition function of the isolated chain is known as Q . The statistical weight factor $e^{2w/kT}$ in Q is replaced by η in our case. Consider that Q is expanded into the power series of η , then, $f(\rho)$ is the coefficient of $\eta^{\rho/2}$. If $f(\rho)\eta^{\rho/2}$ is sufficiently large for some value of η ,

$$\log f(\rho) \cong \log Q - \frac{\rho}{2} \log \eta. \quad (4.1)$$

The mean value of ρ is

$$\bar{\rho} = 2\eta \frac{d \log Q}{d \eta}, \quad (4.2)$$

ρ in Eq. (4.1) may be approximated as $\bar{\rho}$ in Eq. (4.2)

$$\rho = \bar{\rho} \quad (4.3)$$

ρ or η is determined from Eq. (3.6) together with Eq. (4.1)~Eq. (4.3). Particularly, if the concentration of the chain molecules is sufficiently dilute, Eq. (3.6) reduces to

$$\frac{w}{kT} + \frac{d}{d\rho} \log f = 0,$$

or

$$\gamma = \frac{1}{2} \left(\frac{d \log Q}{d \eta} \right)_{v_{\alpha} = 0},$$

This is a satisfactory result because in this case $Q(\eta)$ reduces to the partition function of the isolated chain.

In the following numerical calculations we derive $Q(\eta)$ from the matrix method⁹⁾ which is the extension of the method in the one dimensional Ising model.

§ 5. Discussions and Numerical Calculations

(A) The mixing energy is expressed as

$$\Delta H = z \bar{X} w. \quad (5.1)$$

For the case I (Orr and Guggenheim), $\bar{X}$ is given by Eq. (2.5). According to this equation, the curve ΔH versus $\xi(1-\xi)$ is expected to be a single curve. Contrary to this expectation, the measured curve of the mixing energy of polymethylmethacrylate and trichloroethylene against $\xi(1-\xi)$ is found to be not a single but a closed curve⁵⁾. (Fig. 2). This is explained by Eq. (2.17) in the case II. Because $q_{\alpha'}$ is not constant but changes its value as the concentration increases, the curve ΔH versus $\xi(1-\xi)$ is never a single but a closed curve.

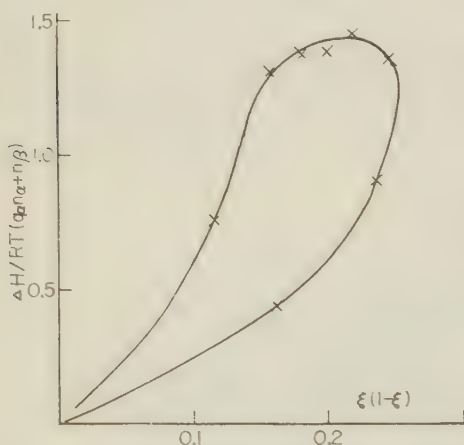


Fig. 2. Values of $\Delta H/RT(q_{\alpha} n_{\alpha} + n_{\beta})$ plotted versus $\xi(1-\xi)$, $z=6$, for solution of polymethylmethacrylate in trichloroethylene. Data from Staverman and Dekking.⁽⁵⁾

(B) The critical mixing point. For the case II, the critical point is given by Eq. (3.11) and Eq. (3.12). These formulas reduce to those of Guggenheim when $\rho_0 = \rho_1 = 0$. So, the case II predicts a larger value of $v_{\alpha,0}$ than the case I. ρ_0 and ρ_1 in the former case are given by

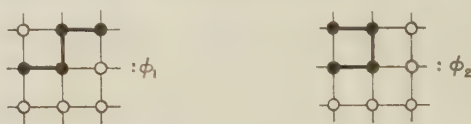
$$\rho_0 = 2\eta \left(\frac{d \log Q}{d \eta} \right)_{v_{\alpha} = 0}, \quad (5.2)$$

$$\rho_1 = 2 \left\{ \left(\frac{d \log Q}{d \eta} \right)_{v_{\alpha} = 0} + \eta \left(\frac{d^2 \log Q}{d \eta^2} \right)_{v_{\alpha} = 0} \right\} \\ \times \eta \left\{ \frac{n-1}{nz} - \frac{2\{z-2-(\rho_0/n)(\eta-1)\}}{z} \right\}. \quad (5.3)$$

The followings are the numerical calculations in some simplified case.

(1) Two dimensional square lattice.

In deriving $Q(\eta)$, "The fundamental configurations" or "vectors" are taken as



Q is given by

$$Q(\eta) = \lambda^n.$$

Where λ is the maximum eigen value of the following matrix,

$$(r_{ij}) = \begin{pmatrix} 1 & 1 \\ \eta & 0 \end{pmatrix}.$$

$$\lambda = \frac{1 + \sqrt{1 + 4\eta}}{2},$$

$$\eta_0 = 1.74,$$

$$\frac{\rho_0}{n} = 0.646, \quad \frac{\rho_1}{n} = -0.091,$$

$$v_{\alpha,0} = \frac{2.67}{\sqrt{n}},$$

Guggenheim's formula gives.

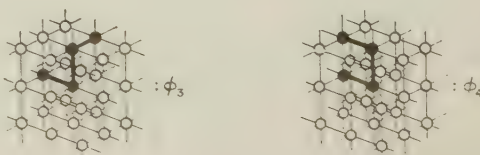
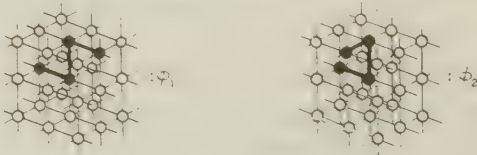
$$v_{\alpha,c,G} = \frac{1.63}{\sqrt{n}}.$$

Flory's theory gives

$$v_{\alpha,c,F} = \frac{1}{\sqrt{n}}.$$

(2) Three dimensional cubic lattice.

"The fundamental vectors" are taken as



$$(\gamma_{ij}) = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ \eta & \eta & \eta & 0 \end{pmatrix},$$

$$\lambda = \frac{3 + \sqrt{9 + 12\eta}}{2},$$

$$\eta_0 = 1.28,$$

$$\frac{\rho_0}{n} = 0.391, \quad \frac{\rho_1}{n} = -0.032,$$

$$v_{\alpha,c} = \frac{1.54}{\sqrt{n}}.$$

Guggenheim's formula gives

$$v_{\alpha,c,G} = \frac{1.34}{\sqrt{n}}.$$

Flory's theory gives

$$v_{\alpha,c,F} = \frac{1}{\sqrt{n}}.$$

Whereas the experimental results^{6)*} show that

$$v_{\alpha,c,\text{exp}} \simeq \frac{2}{\sqrt{n}}.$$

So, our formulas (3.11) and (3.12) predict a better value for $v_{\alpha,c}$ than the previous. But the agreement is not yet satisfactory.

(C) Discussions.

The numerical calculations above show that there yet remain some differences between the theory and the experiments. The reason is partly that the number of "the fundamental configurations" or "vectors" φ_v in calculating $Q(\eta)$ is too small. For the calculation in cubic lattice, only φ_4 has an intrachain interaction. This means that the summation $\rho = \sum_l (l-1) \sum_j Q_{jl}$, the terms $l \geq 3$ are all neglected. If all of these terms are included, ρ will be larger and it makes $v_{\alpha,c}$ larger. Even if ρ is correctly taken in, some unsatisfactory points will yet be remained. For example, the curve of ΔH versus $\xi(1-\xi)$ may not be expected to be such a large loop as

the experiments show. However, if we can construct the theory from the case **III**, further improvements can be expected. Unfortunately this seems to be very complicated.

In addition to the above discussions, the concentration dependency of ρ will yield the valuable informations concerning the concentration dependency of equilibrium extension of the molecular chain.

Acknowledgements

The author expresses his hearty thanks to the chief of our department T. Ichimiya for his permission to publish this article and to Dr. A. Nishioka and other research member of our group for their support of this study.

References

- 1) P. J. Flory: J. Chem. Phys. **10** (1942) 51.
- 2) A. R. Miller: *Theory of Solutions of High Polymers* (Oxford, 1948).
- 3) W. J. C. Orr: Trans. Faraday Soc. **40** (1944) 320.
- 4) E. A. Guggenheim: Proc. Roy. Soc. A, **183** (1944) 203.
- 5) H. Tompa: *Polymer Solutions* (Butterworths Scientific Publication, London, 1956) 144.
- 6) H. Tompa: ditto p. 207.
P. J. Flory: *Principles of Polymer Chemistry* (Cornell Univ. Press, 1953) 546. I. Sakurada, Y. Sakaguchi and Y. Ito: *Kobunshi Kagaku*, **14** 41* (Japanese).
- 7) H. Tompa: ditto p. 174.
- 8) M. L. Huggins: J. Polymer Sci. **16** (1955) 209.
- 9) R. Kubo: J. Phys. Soc. Japan **3** (1948) 119; **4** (1949) 319. H. L. Frish, F. C. Collins and B. Friedman: J. Chem. Phys. **19** (1951) 1402.

* By the study of Sakurada et al., the critical concentrations of partially acetylated polyvinyl alcohols in water show that $v_{\alpha,c} \simeq (1.1/\sqrt{n}) \sim (2.1/\sqrt{n})$ rather than $v_{\alpha,c} \simeq (2/\sqrt{n})$. We will not worry about these results because of the possible abnormal interaction energy such as the hydrogen bonding in this system.

Theory of Electric Birefringence in Dilute Solutions of Tobacco Mosaic Virus

By Sekiko OGAWA and Syoten OKA

*Department of Physics, Faculty of Science,
Tokyo Metropolitan University*

(Received November 27, 1959)

In 1957, O'Konski and Haltner investigated electric birefringence in dilute solutions of tobacco mosaic virus (TMV) in alternating fields. The magnitude of the intrinsic Kerr constant, its frequency dependence and the transient behavior show that the orientation is produced by an induced polarization and that the permanent dipole coupling is negligible. They explained their experimental results by assuming that the transient birefringence follows the first-order rate law.

It is the aim of this paper to calculate the electric birefringence in dilute solutions of TMV in alternating fields with the aid of the distribution functions. The theory is in agreement with the experimental results in that i) the phase retardation of the birefringence relative to the field is proportional to the frequency, ii) the maximum and minimum values of the steady-state birefringence are unity and zero at zero frequency and both values become asymptotically 1/2 with increasing frequency and iii) the magnitude of birefringence decreases rapidly when the frequency is increased beyond 30 kc/sec.

§ 1. Introduction

In 1875, Kerr found that various kinds of isotropic substances were birefringent in strong electric fields. Therefore, this phenomena of electric birefringence is called the "Kerr effect". In this case the substance placed in the electric field behaves as a single crystal with its axis in the direction of the electric field.

In the case of solids, such as glass, there is a possibility of birefringence due to the deformation caused by the electric field.

Since the electric birefringence is observed in liquids such as carbon disulfide and also in gaseous media it is clear that in addition to the indirect effect there is a direct effect which has an influence on the optical properties of a substance.

When an electric field is suddenly applied or removed the mechanical deformation cannot take place without a time delay. Although Kerr effect shows such an effect, it is negligible as compared to that of the mechanical deformation.

Now, if we denote the indices of refraction of plane polarized light waves with electric vectors parallel and perpendicular to the electric field by $n_{\parallel}$ and $n_{\perp}$, respectively, the difference of optical path length between the

two components after the light has passed through a distance l in a substance is given by

$$\Delta = \frac{n_{\parallel} - n_{\perp}}{\lambda_0} l, \quad (1)$$

where λ_0 is the wave length of light in vacuo. According to the experimental results Δ is proportional to the square of the electric field intensity E and the distance l . The following experimental formula results:

$$\Delta = BE^2, \quad (2)$$

B , the Kerr constant, is a material constant which depends on the temperature, the wave length, and the nature of the substance.

The retardation δ , of the parallel component with respect to the perpendicular component is given in radians by

$$\delta = 2\pi \frac{n_{\parallel} - n_{\perp}}{\lambda_0} l. \quad (3)$$

§ 2. Electric Birefringence in TMV Solutions

It is known that rod-like colloids such as vanadium pentoxide and plate-like colloids such as bentonite sol exhibit electric birefringence. Bawden and others¹⁾ also found that TMV solutions are birefringent in an electric field. Further, Lauffer²⁾ and others investigated on the electric birefringence of

TMV, aucuba mosaic and latent mosaic virus. They used an alternating electric field of 60 cycles with voltages ranging from zero to 400 V, and the virus concentration 1-8%. They found positive birefringence of dilute solutions, whereas for concentrated solutions, negative birefringence was observed in the high voltage range. O'Konski and Zimm studied the birefringence of TMV in alternating fields of square pulses independent of frequency. They included the induced dipole moment in their derivation. Berne and Pecora

measured the birefringence of TMV in a static electric field. They found that the birefringence was proportional to the square of the electric field strength.

for the induced birefringence. The electric field strength was the electric field strength. The birefringence was the birefringence. The state caused by the electric field was the electric birefringence.

$$\Delta n = (\Delta n)_0 (1 - e^{-\alpha t}) \tag{4}$$

where $(\Delta n)_0$ is the equilibrium birefringence and D is a constant related to the rotational friction coefficient ζ of the particle.

$$D = kT/\zeta, \tag{5}$$

where k is the Boltzmann constant and T is absolute temperature.

Benoit also made calculations for the case where a static field is applied after $t=0$. In this case the rather complicated expression for the birefringence is

$$\begin{aligned} \frac{1}{c} \frac{\Delta n}{n} = & \frac{2\pi}{15} (g_1 - g_2) \frac{1}{n^2} \\ & \times \left[E^2 \left\{ P + Q - \frac{3}{2} P e^{-r_1 D t} + \left(\frac{P}{2} - Q \right) e^{-r_2 D t} \right\} \right. \\ & + E^4 \left\{ \frac{Q^2}{21} - \frac{P^2}{15} + \frac{19}{105} P Q - \frac{3}{28} P Q e^{-r_1 D t} \right. \\ & \left. \left. + \left(\frac{P^2}{15} - \frac{Q^2}{21} - \frac{31}{420} P Q \right) e^{-r_2 D t} \right\} \right], \tag{6} \end{aligned}$$

where c is the concentration, n is the index of refraction in the absence of the electric

field and P , Q , r_1 and r_2 are defined as follows

$$\left. \begin{aligned} P &= \left(\frac{\mu}{kT} \right)^2, \\ Q &= \frac{v(g_1 - g_2)}{kT}, \end{aligned} \right\} \tag{7}$$

$$\left. \begin{aligned} r_1 &= 2 + E^2 \left(\frac{P}{5} - \frac{2}{5} Q \right), \\ r_2 &= E^2 \left(\frac{P}{5} + \frac{2}{7} Q \right). \end{aligned} \right\} \tag{8}$$

the volume of the particle, the permanent dipole moment and g_1 and g_2 are the anisotropy of the polarizability. Eqs. (4) and (6) are valid under the following assumptions.

$$\alpha = \frac{P}{Q}. \tag{9}$$

For weak electric fields, the permanent dipole moment is negligible, and Eq. (6) reduces to

$$\Delta n = (\Delta n)_0 (1 - e^{-\alpha t}) \tag{10}$$

for weak electric fields. In his case the induced birefringence becomes symmetric as in Fig. 1. When the electric field is applied, the birefringence increases and then decays to zero.

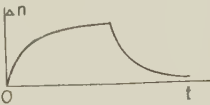


Fig. 1.

For $\alpha \rightarrow \infty$ Eq. (6) becomes

$$\Delta n = (\Delta n)_0 \left(1 - \frac{3}{2} e^{-\alpha D t} + \frac{1}{2} e^{-\alpha^2 D t} \right), \tag{11}$$

O'Konski and Haltner^{5,6)} studied the effects of field strength, TMV and electrolyte concentrations and pH on the electric birefringence of dilute TMV solutions employing pulsed sine waves. Measurements were made with reversing square pulse and exponentially decaying pulse fields.

From the sign and magnitude of the intrinsic Kerr constant, its frequency dependence and the transient behavior, they concluded that the orientation of TMV particles is not produced by a permanent dipole moment, but by an induced polarization. They also found that the value of Kerr constant is about fifty times greater than that expected from electronic and atomic polarizations. These authors proposed that the large electric anisotropy arises because of the polarizability

of the ion atmosphere. They interpreted the experimental results in terms of models having conductive surface as a result of the relatively high local concentration of counterions at low ionic strength.

O'Konski and Haltner explained their experimental results on the electric birefringence of dilute TMV solutions in the case of alternating fields by assuming that the transient birefringence follows the same first-order rate law both for the build-up and decay of the electric fields. It is the purpose of this paper to calculate the electric birefringence for the alternating field without such assumptions.

§ 3. Electric Birefringence in Solutions of Anisotropic Colloidal Particles

Let us consider the fundamental equations of electric birefringence in a non-homogeneous system in which anisotropic colloidal particles are dispersed in an isotropic liquid⁷⁾. We shall first make the following assumptions: (i) the concentration of the solution is so dilute that the interaction of the particles may be neglected; (ii) the particles are all identical (iii) the particle is very small compared to the wavelength of light; (iv) the particle is a rigid ellipsoid of rotation and the geometrical axes coincide with the optical and the electrical axes; (v) the permanent dipole moment μ is in the direction of axis of rotation; (vi) the particle has no charge; (vii) the solvent is isotropic; (viii) the influence of the ion atmosphere is negligible.

The polarization $\mathbf{P}$ induced in the system by the electric vector of the incident light wave $\mathbf{E}$ is given by

$$\mathbf{P} = \mathbf{P}_i + \Sigma \mathbf{p}, \quad (12)$$

where $\mathbf{P}_i$ is the polarization of the solvent, and $\Sigma \mathbf{p}$ indicates the sum of the polarizations of all the particles in unit volume. Therefore, $\bar{\Sigma \mathbf{p}}$ represents the mean value of $\Sigma \mathbf{p}$ with respect to the given orientation of the particles. Let the components of $\mathbf{E}$ parallel and perpendicular to the axis of symmetry of the particle be denoted by E_1 and E_2 , respectively; then the components p_1 and p_2 of $\mathbf{p}$ parallel and perpendicular, respectively, to the axis of symmetry of the particle are given by

$$\left. \begin{aligned} p_1 &= v g_1 E_1, \\ p_2 &= v g_2 E_2, \end{aligned} \right\} \quad (13)$$

where v is the volume of the particle. g_1 and

g_2 are dimensionless constants defined by the following equations

$$\left. \begin{aligned} g_1 &= \frac{n_1^2 - n_i^2}{4\pi + ((n_1^2 - n_i^2)/n_i^2)L_1}, \\ g_2 &= \frac{n_2^2 - n_i^2}{4\pi + ((n_2^2 - n_i^2)/n_i^2)L_2}, \end{aligned} \right\} \quad (14)$$

where n_1 and n_2 are the indices of refraction parallel and perpendicular, respectively, to the axis of symmetry of the particle, and n_i is the index of refraction of the solvent. L_1 and L_2 are dimensionless constants defined by the following equations

$$\left. \begin{aligned} L_1 &= \frac{4}{3} \pi (1 - 2e), \\ L_2 &= \frac{4}{3} \pi (1 - e). \end{aligned} \right\} \quad (15)$$

If we denote by $2a_1$ and $2a_2$ the length of the principal axes parallel and perpendicular, respectively, to the axis of symmetry of the particle, then e is the function of p ($=a_1/a_2$) as follows

$$\begin{aligned} e &= \frac{1}{4(p^2 - 1)} \left[2p^2 + 4 - \frac{3p}{\sqrt{p^2 - 1}} \right. \\ &\quad \times \log \frac{p + \sqrt{p^2 - 1}}{p - \sqrt{p^2 - 1}} \left. \right], \quad p > 1 \\ &= \frac{p'^2}{4(p'^2 - 1)} \left[-\frac{2}{p'^2} + 4 \right. \\ &\quad \left. + \frac{6}{\sqrt{p'^2 - 1}} \tan^{-1} \sqrt{p'^2 - 1} \right], \\ p' &\equiv \frac{1}{p} > 1. \end{aligned} \quad (16)$$

If $p > 1$, the particle is a prolate spheroid; if $p < 1$ the particle is termed an oblate spheroid whereas $p = 1$ corresponds to a sphere. From

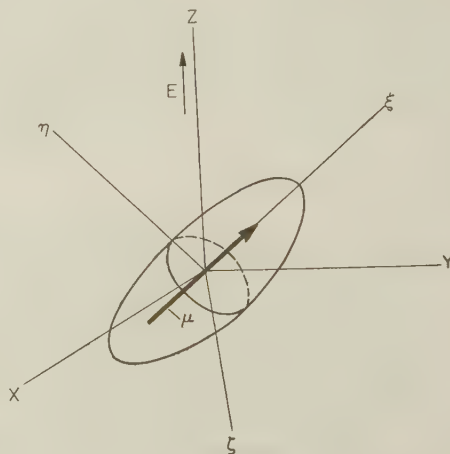


Fig. 2.

Eq. (16) it can be seen that $e \geq 0$ depending on $p \geq 1$ and the value of e is always in the region $-1 < e < \frac{1}{2}$.

Considering a fixed rectangular coordinate axes, X, Y, Z , assume that the electric vector of the incident light $\mathbf{E}$ is in the direction of the X axis. Then the X component of Eq. (17) is given by Eq. (18).

$$n^2 \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}, \quad (17)$$

$$4\pi P_X = (n_{XX}^2 - 1)E_X, \quad (18)$$

n_{XX}^2 is the XX component of the tensor n^2 . From Eq. (12) P_X is given by

$$P_X = P_{IX} + \overline{\Sigma p_X}. \quad (19)$$

If ξ is the axis of symmetry of the particle and η and ζ are the axes perpendicular to ξ , then p_X is given by

$$p_X = p_1 \cos(\xi X) + p_\eta \cos(\eta X) + p_\zeta \cos(\zeta X), \quad (20)$$

where

$$p_1 = v g_1 E_1,$$

$$p_\eta = v g_2 E_\eta,$$

$$p_\zeta = v g_2 E_\zeta,$$

and

$$E_1 = E_\xi = E_X \cos(\xi X),$$

$$E_\eta = E_X \cos(\eta X),$$

$$E_\zeta = E_X \cos(\zeta X).$$

Thus we have

$$\left. \begin{aligned} p_1 &= v g_1 E_X \cos(\xi X), \\ p_\eta &= v g_2 E_X \cos(\eta X), \\ p_\zeta &= v g_2 E_X \cos(\zeta X), \end{aligned} \right\} \quad (21)$$

Substituting Eqs. (21) into Eq. (20) one gets the final form of p_X ,

$$p_X = v g_1 E_X \cos^2(\xi X) + v g_2 E_X \{1 - \cos^2(\xi X)\}$$

The expressions for p_Y and p_Z are obtained in a similar manner. Thus we have

$$\left. \begin{aligned} p_X &= v \{g_2 + (g_1 - g_2) \cos^2(\xi X)\} E_X, \\ p_Y &= v (g_1 - g_2) \cos(\xi X) \cos(\xi Y) E_X, \\ p_Z &= v (g_1 - g_2) \cos(\xi X) \cos(\xi Z) E_X. \end{aligned} \right\} \quad (22)$$

n_{XX}^2 can be obtained from Eqs. (18) and (19), and the other components of n^2 are obtained in an analogous fashion as given in Eq. (21).

$$\left. \begin{aligned} n_{XX}^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi X)}\}, \\ n_{YY}^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi Y)}\}, \\ n_{ZZ}^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi Z)}\}, \\ n_{XY}^2 &= n_{YX}^2 = 4\pi\phi (g_1 - g_2) \times \overline{\cos(\xi X) \cos(\xi Y)}, \\ n_{YZ}^2 &= n_{ZY}^2 = 4\pi\phi (g_1 - g_2) \times \overline{\cos(\xi Y) \cos(\xi Z)}, \\ n_{ZX}^2 &= n_{XZ}^2 = 4\pi\phi (g_1 - g_2) \times \overline{\cos(\xi Z) \cos(\xi X)}. \end{aligned} \right\} \quad (23)$$

ϕ is equal to Nv , where N is the number of particles in unit volume of the solution. The bar over $\cos^2(\xi X)$ represents the mean value of $\cos^2(\xi X)$ over all possible orientations of the particle. As seen from Eq. (23) n^2 is a symmetric tensor. If we take the principal axes x, y and z and denote the principal indices of refraction by n_x, n_y and n_z , then Eq. (23) become:

$$\left. \begin{aligned} n_x^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi x)}\}, \\ n_y^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi y)}\}, \\ n_z^2 &= n_l^2 + 4\pi\phi \times \{g_2 + (g_1 - g_2) \overline{\cos^2(\xi z)}\}. \end{aligned} \right\} \quad (24)$$

When the electric field is applied, the relationships $\cos^2(\xi x) = \cos^2(\xi y) = \cos^2(\xi z)$ does not hold and the solution becomes optically anisotropic. The electric birefringence Δn for light traveling in the y direction is measured by $(n_x - n_z)$. When the concentration of the solution is very dilute ϕ is considerably small and Eq. (24) reduces to

$$\Delta n = \phi \frac{2\pi(g_1 - g_2)}{n} \{\overline{\cos^2(\xi z)} - \overline{\cos^2(\xi x)}\}. \quad (25)$$

In the absence of an electric field $\overline{\cos^2(\xi x)}$ is equal to $1/3$, and according to Eq. (24) the index of refraction is given by

$$n^2 = n_l^2 + 4\pi\phi \left\{ g_2 + \frac{1}{3} (g_1 - g_2) \right\}. \quad (26)$$

As seen from Eq. (25) Δn consists of two factors, $(g_1 - g_2)$, the "optical anisotropic factor" and $\{\overline{\cos^2(\xi z)} - \overline{\cos^2(\xi x)}\}$, the "orientation factor".

§ 4. Distribution Function

It is necessary for the calculation of the orientation factor to obtain the distribution function which determines the orientation of the particle. If we denote by $f d\Omega$ the probability that the axis of symmetry of the particle is in the infinitesimal solid angle $d\Omega$, then the distribution function f is a function of θ , φ and t , and satisfies the following differential equation:

$$\frac{\zeta}{kT} \frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \times \frac{\partial}{\partial \theta} \left\{ \sin \theta \left(\frac{\partial f}{\partial \theta} - \frac{M}{kT} f \right) \right\}, \quad (27)$$

where ζ is the coefficient of rotational friction around the minor axes. M is the couple due to the external electric field E and consists of the moment $(-\mu E \sin \theta)$ due to the permanent dipole and the moment of the induced dipole M' , that is

$$M = -\mu E \sin \theta + M', \quad (28)$$

where

$$M' = -p_1 E \sin \theta + p_2 E \cos \theta. \quad (29)$$

p_1 and p_2 are the component P , the dipole moment of the particle induced by the electric field E , and corresponding to Eq. (13) we have

$$\left. \begin{aligned} p_1 &= v g_{e1} E_1, \\ p_2 &= v g_{e2} E_2. \end{aligned} \right\} \quad (30)$$

g_{e1} and g_{e2} are give by

$$\left. \begin{aligned} g_{e1} &= \frac{\epsilon_1 - \epsilon_l}{4\pi + ((\epsilon_1 - \epsilon_l)/\epsilon_l)L_1}, \\ g_{e2} &= \frac{\epsilon_2 - \epsilon_l}{4\pi + ((\epsilon_2 - \epsilon_l)/\epsilon_l)L_2}, \end{aligned} \right\} \quad (31)$$

where ϵ_l is the dielectric constant of the solvent, ϵ_1 and ϵ_2 are the dielectric constants parallel and perpendicular, respectively, to the axis of symmetry of the particle. L_1 and L_2 are the same as in Eq. (14). Substituting Eq. (30) into Eq. (29) we have

$$M' = -v(g_{e1} - g_{e2})E^2 \sin \theta \cos \theta.$$

Thus, from Eq. (28)

$$M = -\mu E \sin \theta - v(g_{e1} - g_{e2}) \times E^2 \sin \theta \cos \theta. \quad (32)$$

Substituting Eq. (32) into Eq. (27) we have

$$\frac{\zeta}{kT} \frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \times \left[\sin \theta \left\{ \frac{\partial f}{\partial t} + \frac{v(g_{e1} - g_{e2})E^2}{kT} \right\} \right]$$

$$\times f \sin \theta \cos \theta + \frac{\mu E}{kT} f \sin \theta \left. \right\}. \quad (33)$$

If we put for simplicity,

$$\left. \begin{aligned} p &= \frac{\mu E}{kT}, \\ q &= \frac{v(g_{e1} - g_{e2})}{kT} E^2, \end{aligned} \right\} \quad (34)$$

$$\tau = \frac{\zeta}{2kT}, \quad (35)$$

Eq. (33) becomes

$$2\tau \frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \times \left(\sin \theta \frac{\partial f}{\partial \theta} + p f \sin^2 \theta + g f \sin^2 \theta \cos \theta \right). \quad (36)$$

If we put $\cos \theta = u$, Eq. (36) can be rewritten as follows:

$$2\tau \frac{\partial f}{\partial t} = (1 - u^2) \frac{\partial^2 f}{\partial u^2} - 2u \frac{\partial f}{\partial u} - (1 - u^2)(p + qu) \frac{\partial f}{\partial u} + f \{ 2pu + q(3u^2 - 1) \}. \quad (37)$$

To obtain the distribution function f , it is convenient that f is expanded into Legendre's functions, P_n , that is

$$f(u, t) = \sum_{n=0}^{\infty} \varphi_n(t) P_n(u). \quad (38)$$

Substituting Eq. (38) into Eq. (37) and making use of the following relations

$$\left. \begin{aligned} (1 - u^2) P_n''(u) - 2u P_n'(u) + n(n+1) P_n(u) &= 0, \\ (1 - u^2) P_n'(u) &= n P_{n-1}(u) - nu P_n(u), \\ (2n+1) u P_n(u) &= (n+1) P_{n+1}(u) + n P_{n-1}(u), \end{aligned} \right\} \quad (39)$$

we get

$$\begin{aligned} 2\tau \sum \varphi_n'(t) P_n(u) &= \sum \varphi_n'(t) \left[-n(n+1) P_n \right. \\ &\quad - P \frac{n(n+1)}{2n+1} P_{n-1} \\ &\quad + P \frac{(n+1)(n+2)}{2n+1} P_{n+1} \\ &\quad \left. + q \frac{(n+1)(n+2)(n+3)}{(2n+1)(2n+3)} P_{n+2} \right] \end{aligned}$$

$$-q \frac{n(n-1)(n-2)}{4n^2-1} P_{n-2} - q \left\{ \frac{n^2(n-2)}{4n^2-1} - \frac{(n+1)^2(n+3)}{(2n+1)(2n+3)} + 1 \right\} P_n \quad (40)$$

Multiplying both sides of Eq. (40) by $P_m(u)$ and integrating it from -1 to 1 with respect to u , we obtain

$$2\tau\varphi_m'(t) = -\varphi_m \left[m(m+1) + q \left\{ 1 - \frac{m^2(m-2)}{4m^2-1} - \frac{(m+1)^2(m+3)}{(2m+1)(2m+3)} \right\} \right] + \varphi_{m-1} p \frac{m(m+1)}{2m-1} - \varphi_{m+1} p \frac{m(m+1)}{2m+3} + \varphi_{m-2} q \frac{m(m^2-1)}{(2m-1)(2m-3)} + \varphi_{m+2} q \frac{m(m+1)(m+2)}{(2m+3)(2m+5)} \quad (m=0, 1, 2, \dots) \quad (41)$$

since

$$\left. \begin{aligned} \int_{-1}^1 P_m(u) P_n(u) du &= 0, & n \neq m \\ &= \frac{2}{2m+1}, & n = m. \end{aligned} \right\} \quad (42)$$

If we put $m=0, 1$ and 2 in Eq. (42) we have

$$2\tau\varphi_0'(t) = 0, \quad (43)$$

$$2\tau\varphi_1'(t) = 2p\varphi_0 - 2\varphi_1 \left(1 + \frac{2}{15}q \right) p - \frac{2}{5}\varphi_2 - \frac{6}{35}q\varphi_3, \quad (44)$$

$$2\tau\varphi_2'(t) = 2q\varphi_0 + 2p\varphi_1 - 2\varphi_2 \left(3 - \frac{1}{7}q \right) - \frac{6}{7}p\varphi_3 - \frac{8}{21}q\varphi_4. \quad (45)$$

From Eq. (43) it is seen that $\varphi_0(t)$ is a constant. This constant is equal to $1/4\pi$, since the condition

$$\int f d\Omega = 1$$

must be satisfied. Thus,

$$\varphi_0(t) = \frac{1}{4\pi}. \quad (46)$$

§ 5. Mean Value of φ_2 for a Static Field

At equilibrium under a static field, the

distribution function f is independent of time. Therefore Eqs. (44) and (45) become

$$\left. \begin{aligned} \frac{p}{2\pi} - 2\varphi_1 \left(1 + \frac{2}{15}q \right) - \frac{2}{5}p\varphi_2 &= 0, \\ \frac{q}{2\pi} + 2p\varphi_1 - 2\varphi_2 \left(3 - \frac{1}{7}q \right) &= 0, \end{aligned} \right\}$$

where the terms φ_3 and φ_4 are neglected. Eliminating φ_1 from the above equations we obtain

$$\varphi_2 = \frac{\frac{p^2}{2\pi} + \frac{q}{2\pi} \left(1 + \frac{2}{15}q \right)}{\frac{2}{5}p^2 + 2 \left(3 - \frac{q}{7} \right) \left(1 + \frac{2}{15}q \right)}.$$

For small values of p and q , φ_2 becomes

$$\varphi_2 = \frac{1}{12\pi} (p^2 + q)$$

or from Eq. (34)

$$\varphi_2 = -\frac{E^2}{12\pi} \left[\left(\frac{\mu}{kT} \right)^2 + \frac{v(g_{e1} - g_{e2})}{kT} \right]. \quad (47)$$

§ 6. φ_2 for an Alternating Field

We assume that an alternating field is applied from $t=0$:

$$E = E_0 \sin \omega t. \quad (t \geq 0) \quad (48)$$

Substituting Eq. (48) into Eq. (34) we have

$$\left. \begin{aligned} p &= \varepsilon \sin \omega t, \\ q &= \beta \varepsilon \sin^2 \omega t, \end{aligned} \right\} \quad (49)$$

where ε and β are defined, for simplicity, as follows:

$$\varepsilon = \frac{\mu E_0}{kT}, \quad (50)$$

$$\beta = \frac{v(g_{e1} - g_{e2})kT}{\mu^2}, \quad (51)$$

Substituting Eq. (49) into (44) and neglecting the terms of φ_3 and φ_4 we have

$$\left. \begin{aligned} 2\tau\varphi_1' - \frac{\varepsilon}{2\pi} \sin \omega t \\ + 2\varphi_1 \left(1 + \frac{2}{15}\beta\varepsilon^2 \sin^2 \omega t \right) \\ + \frac{2}{5}\varepsilon \sin \omega t \cdot \varphi_2 &= 0, \\ 2\tau\varphi_2' - \frac{1}{2\pi}\beta\varepsilon^2 \sin^2 \omega t \\ - 2\varepsilon \sin \omega t \cdot \varphi_1 \\ + 2 \left(3 - \frac{1}{7}\beta\varepsilon^2 \sin^2 \omega t \right) \varphi_2 &= 0. \end{aligned} \right\} \quad (52)$$

If ε is small, φ_1 and φ_2 can be written as

follows:

$$\left. \begin{aligned} \varphi_1 &= \varphi_{10} + \varphi_{11}\varepsilon + \varphi_{12}\varepsilon^2, \\ \varphi_2 &= \varphi_{20} + \varphi_{21}\varepsilon + \varphi_{22}\varepsilon^2. \end{aligned} \right\} \quad (53)$$

Substituting Eq. (53) into Eq. (52) and putting the coefficient of ε^0 , ε , and ε^2 equal to zero, we find:

$$2\tau\varphi_{10}' + 2\varphi_{10} = 0, \quad (54)$$

$$\begin{aligned} 2\tau\varphi_{11}' - \frac{1}{2\pi} \sin \omega t + 2\varphi_{11} \\ + \frac{2}{5} \varphi_{20} \sin \omega t = 0, \end{aligned} \quad (55)$$

$$\begin{aligned} 2\tau\varphi_{12}' + 2\left(\frac{2}{15}\beta\varphi_{10} \sin^2 \omega t + \varphi_{12}\right) \\ + \frac{2}{5} \varphi_{21} \sin \omega t = 0, \end{aligned} \quad (56)$$

$$2\tau\varphi_{20}' + 6\varphi_{20} = 0, \quad (57)$$

$$2\tau\varphi_{21}' - 2\varphi_{10} \sin \omega t + 6\varphi_{21} = 0, \quad (58)$$

$$\begin{aligned} 2\tau\varphi_{22}' - \frac{1}{2\pi} \beta \sin^2 \omega t - 2 \sin \omega t \cdot \varphi_{11} \\ + 2\left(3\varphi_{22} - \frac{1}{7}\beta\varphi_{20} \sin^2 \omega t\right) = 0. \end{aligned} \quad (59)$$

From Eq. (54)

$$\varphi_{10} = A e^{-t/\tau}.$$

Since f is equal to $1/4\pi$ when t is zero, $\varphi_0(0)$ is equal to $1/4\pi$. Therefore, $\varphi_1(0) = \varphi_2(0) = 0$, $\varphi_{10}(0) = \varphi_{11}(0) = \varphi_{12}(0) = 0$. From these relationships A must be equal to zero, and we have

$$\varphi_{10} = 0. \quad (60)$$

From Eq. (57) we get the following equation

$$\varphi_{20} = B e^{-3t/\tau}.$$

Since $\varphi_{20}(0) = \varphi_{21}(0) = \varphi_{22}(0) = 0$, B vanishes and

$$\varphi_{20} = 0. \quad (61)$$

Substituting Eq. (61) into Eq. (55) we obtain

$$2\tau\varphi_{11}' + 2\varphi_{11} = \frac{1}{2\pi} \sin \omega t.$$

Thus the solution is

$$\begin{aligned} \varphi_{11} &= C e^{-t/\tau} + \frac{1}{4\pi} \frac{1}{1 + \omega^2 \tau^2} \\ &\quad \times (\sin \omega t - \omega \tau \cos t). \end{aligned}$$

Since $\varphi_{11}(0) = 0$, C is given by

$$C = \frac{1}{4\pi} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2}.$$

Therefore

$$\begin{aligned} \varphi_{11} &= \frac{1}{4\pi} \frac{1}{1 + \omega^2 \tau^2} (\omega \tau e^{-t/\tau} \\ &\quad + \sin \omega t - \omega \tau \cos \omega t). \end{aligned} \quad (62)$$

Substituting Eq. (60) into Eq. (58) we have $\varphi_{21} = E e^{-3t/\tau}$. Since $E = 0$ we have $\varphi_{21}(0) = 0$. Thus

$$\varphi_{21}(0) = 0. \quad (63)$$

Substituting Eq. (61) and Eq. (62) into Eq. (59),

$$\begin{aligned} 2\tau\varphi_{22}' + 6\varphi_{22} &= \frac{1}{2\pi} \beta \sin^2 \omega t \\ &+ \frac{1}{2\pi} \frac{1}{1 + \omega^2 \tau^2} (\omega \tau e^{-t/\tau} \\ &\quad \times \sin \omega t + \sin^2 \omega t \\ &\quad - \omega \tau \cos \omega t \cdot \sin \omega t). \end{aligned}$$

The solution is given by

$$\begin{aligned} \varphi_{22} &= \frac{\beta}{24\pi} \left[1 - \frac{1}{1 + 4\omega^2 \tau^2 / 9} \right. \\ &\quad \times \left(\cos 2\omega t + \frac{2}{3} \omega \tau \cdot \sin \omega t \right) \Big] \\ &+ \frac{\omega \tau}{8\pi} e^{-t/\tau} \frac{1}{(1 + \omega^2 \tau^2)(1 + \omega^2 \tau^2 / 4)} \\ &\quad \times \left(\sin \omega t - \frac{\omega \tau}{2} \cos \omega t \right) \\ &+ \frac{1}{24\pi} \frac{1}{1 + \omega^2 \tau^2} \left[1 - \frac{1}{1 + 4\omega^2 \tau^2 / 9} \right. \\ &\quad \times \left(\cos 2\omega t + \frac{2\omega \tau}{3} \sin \omega t \right) \Big] \\ &- \frac{1}{24\pi} \frac{\omega \tau}{(1 + \omega^2 \tau^2)(1 + 4\omega^2 \tau^2 / 9)} \\ &\quad \times \left(\sin 2\omega t - \frac{2}{3} \omega \tau \cos 2\omega t \right) \\ &\quad + F e^{-3t/\tau}. \end{aligned}$$

For the special case $t \gg 2\tau$, the terms of $\exp(-t/\tau)$ and $\exp(-3t/\tau)$ can be neglected and the following approximate relationship holds:

$$\begin{aligned} \varphi_{22} &= \frac{\beta}{24\pi} \left[1 - \frac{1}{1 + 4\omega^2 \tau^2 / 9} \right. \\ &\quad \times \left(\cos 2\omega t + \frac{2}{3} \omega \tau \sin 2\omega t \right) \Big] \\ &+ \frac{1}{24\pi} \frac{1}{1 + \omega^2 \tau^2} \left[1 - \frac{1}{1 + 4\omega^2 \tau^2 / 9} \right. \\ &\quad \times \left(\cos 2\omega t + \frac{2}{3} \omega \tau \sin 2\omega t \right) \Big] \\ &- \frac{1}{24\pi} \frac{\omega \tau}{(1 + \omega^2 \tau^2)(1 + 4\omega^2 \tau^2 / 9)} \\ &\quad \times \left(\sin 2\omega t - \frac{2}{3} \omega \tau \cos 2\omega t \right). \end{aligned}$$

Now, introducing φ according to the following equation

$$\tan \varphi = \frac{2\omega\tau}{3}, \quad (64) \quad \text{If}$$

then φ_{22} can be rewritten as follows:

$$\begin{aligned} \varphi_{22} = & \frac{1}{24\pi} \left(\beta + \frac{1}{1+\omega^2\tau^2} \right) \\ & - \frac{\beta}{24\pi} \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \\ & \times \cos(2\omega t - \varphi) - \frac{1}{24\pi} \cdot \frac{1}{1+\omega^2\tau^2} \\ & \times \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} [\cos(2\omega t - \varphi) \\ & + \omega\tau \sin(2\omega t - \varphi)]. \end{aligned}$$

Also if

$$\tan \gamma = \omega\tau, \quad (65)$$

then we have

$$\begin{aligned} \varphi_{22} = & \frac{1}{24\pi} \left(\beta + \frac{1}{1+\omega^2\tau^2} \right) \\ & - \frac{\beta}{24\pi} \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \\ & \times \cos(2\omega t - \varphi) - \frac{1}{24\pi} \cdot \frac{1}{(1+\omega^2\tau^2)^{1/2}} \\ & \times \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \cdot \cos(2\omega t - \varphi - \gamma). \end{aligned}$$

The second and third terms on the right-hand side of the above equation can be rearranged as follows:

$$\begin{aligned} \varphi_{22} = & \frac{1}{24\pi} \left(\beta + \frac{1}{1+\omega^2\tau^2} \right) \\ & - C \cos(2\omega t - \varphi - \psi), \end{aligned}$$

where C and ψ are given by

$$\left. \begin{aligned} C^2 = & \frac{1}{(24\pi)^2} \frac{1}{(1+\omega^2\tau^2/9)} \beta^2 \\ & + \frac{1}{1+\omega^2\tau^2} + 2\beta \frac{1}{1+\omega^2\tau^2}, \\ \tan \psi = & \frac{\omega\tau}{1+\beta(1+\omega^2\tau^2)}. \end{aligned} \right\} \quad (66)$$

By making use of Eqs. (53), (61) and (63) we obtain $\varphi_2 = \varepsilon^2 \varphi_{22}$, or from Eqs. (50) and (51) we have

$$\begin{aligned} \frac{\varphi_2}{E_0^2} = & \frac{1}{24\pi} \left[\frac{(\mu/kT)^2}{1+\omega^2\tau^2} \right. \\ & + \frac{v(g_{e1}-g_{e2})}{kT} \left. \right] - \frac{1}{24\pi} \cdot \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \\ & \times \left[\frac{v^2(g_{e1}-g_{e2})^2}{(kT)^2} + \frac{2v(g_{e1}-g_{e2})\mu^2}{(kT)^3(1+\omega^2\tau^2)} \right. \\ & \left. + \frac{(\mu/kT)^4}{1+\omega^2\tau^2} \right]^{1/2} \cdot \cos(2\omega t - \varphi - \psi). \quad (67) \end{aligned}$$

$$\beta = \frac{v(g_{e1}-g_{e2})kT}{\mu^2} \rightarrow \infty, \quad \psi \rightarrow 0$$

and the following relation is obtained:

$$\begin{aligned} \frac{\varphi_2}{E_0^2} = & \frac{1}{24\pi} \frac{v(g_{e1}-g_{e2})}{kT} \\ & \times \left[1 - \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \cdot \cos(2\omega t - \varphi) \right]. \quad (68) \end{aligned}$$

§ 7. Calculation of Electric Birefringence

We have shown in section 3 that the birefringence Δn is given by Eq. (25). Now, we shall calculate the orientation factor

$$\overline{\cos^2(\xi z)} - \overline{\cos^2(\xi x)}.$$

From the definition, $\overline{\cos^2(\xi z)}$ is expressed, in terms of the distribution function f , as follows:

$$\overline{\cos^2(\xi z)} = \int \cos^2(\xi z) f d\Omega$$

or

$$\overline{\cos^2(\xi z)} = \int_0^\pi \int_0^{2\pi} f \cos^2\theta \sin\theta d\theta d\varphi.$$

From Eq. (46) the expression (38) of the distribution function is generally given by

$$f(u, t) = \frac{1}{4\pi} + \sum_{n=1}^{\infty} \varphi_n(t) P_n(u), \quad (u = \cos\theta). \quad (69)$$

Substituting this relation into the above equation we have

$$\overline{\cos^2(\xi z)} = \frac{1}{3} + 2\pi \sum \varphi_n(t) \int_{-1}^1 u^2 P_n(u) du,$$

or from

$$u = \frac{2}{3} p_2(u) + \frac{1}{3}$$

and Eq. (41),

$$\overline{\cos^2(\xi z)} = \frac{1}{3} + \frac{8\pi}{15} \varphi_2. \quad (70)$$

Similarly $\overline{\cos^2(\xi x)}$ can be calculated, namely

$$\overline{\cos^2(\xi x)} = \iint \sin^2\theta \cos^2\varphi + \sin\theta d\theta d\varphi.$$

Substituting Eq. (69) into this relation we have

$$\overline{\cos^2(\xi x)} = \frac{1}{3} - \frac{4}{15} \pi \varphi_2. \quad (71)$$

From Eqs. (70) and (71)

$$\overline{\cos^2(\xi z)} - \overline{\cos^2(\xi x)} = \frac{4}{5} \pi \varphi_2. \quad (72)$$

Consequently it is found that the orientation factor is determined only by φ_2 . Substituting Eq. (72) into the equation of birefringence Eq. (25) we obtain

$$\Delta n = \frac{8\pi^2}{5n} \phi (g_1 - g_2) \varphi_2. \quad (73)$$

Thus the retardation δ is expressed, according to Eq. (3), as follows:

$$\delta = \frac{16\pi^8 l \phi}{5\lambda_0 n} (g_1 - g_2) \varphi_2. \quad (74)$$

§ 8. Electric Birefringence for Alternating Fields

The retardation δ for the alternating fields $E = E_0 \sin \omega t$ is obtained by substituting Eq. (67) into Eq. (74). If we put for simplicity

$$\left. \begin{aligned} L &= \frac{(\mu/kT)^2}{1+\omega^2\tau^2} + \frac{v(g_{e1}-g_{e2})}{kT}, \\ M &= \left[\frac{v^2(g_{e1}-g_{e2})^2}{(kT)^2} + \frac{2v(g_{e1}-g_{e2})}{kT} \right. \\ &\quad \left. \times \frac{(\mu/kT)^2}{1+\omega^2\tau^2} + \frac{(\mu/kT)^4}{1+\omega^2\tau^2} \right]^{1/2} \end{aligned} \right\} \quad (75)$$

Then we have

$$\delta = \frac{2}{5} \pi^2 \frac{l \phi}{\lambda_0 n} (g_1 - g_2) E_0^2 L \times \left[1 - \frac{M}{L} \frac{1}{(1-4\omega^2\tau^2/9)^{1/2}} \cos(2\omega t - \varphi - \psi) \right]. \quad (76)$$

Thus δ consists of two terms: one is independent of time and the other changes periodically with time. Let δ_0 be the mean value of δ over one period or over a time interval sufficiently large compared to one period. The second term on the right-hand side of Eq. (76) vanishes and we have

$$\delta_0 = \frac{2\pi^2 l \phi}{15 \lambda_0 n} (g_1 - g_2) E_0^2 L. \quad (77)$$

By making use of δ_0 , Eq. (76) is rewritten as follows:

$$\delta = \delta_0 \left[1 - \frac{M}{L} \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \times \cos(2\omega t - \varphi - \psi) \right]. \quad (78)$$

Now, if one denotes the maximum and minimum values of δ by δ_M it follows that

$$\delta_M = \delta_0 \left[1 \pm \frac{M}{L} \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \right]. \quad (79)$$

The phase difference δ_S for a static field E can also be calculated. If one substitutes Eq.

(47) into Eq. (74)

$$\delta_S = A E^2, \quad (80)$$

$$A = \frac{4\pi^2 l \phi}{15 \lambda_0 n} (g_1 - g_2) \times \left[\left(\frac{\mu}{kT} \right)^2 + \frac{v(g_{e1} - g_{e2})}{kT} \right]. \quad (81)$$

By making use of the above relation δ_0 is given by

$$\delta_0 = \frac{A E_0^2}{2} \frac{1}{1+\alpha} \left(1 + \frac{\alpha}{1+\omega^2\tau^2} \right) \quad (82)$$

where

$$\alpha = \frac{\mu^2}{v(g_{e1} - g_{e2}) kT} \left(= \frac{1}{\beta} \right) \quad (83)$$

for simplicity. Then, from (79) δ_M is rewritten as follows:

$$\begin{aligned} \frac{\delta_M}{A E_0^2} &= \frac{1}{2} \cdot \frac{1}{1+\alpha} \left(1 + \frac{\alpha}{1+\omega^2\tau^2} \right) \\ &\times \left[1 \pm \frac{(1+2\alpha/(1+\omega^2\tau^2) + \alpha^2/(1+\omega^2\tau^2))^{1/2}}{1+\alpha/(1+\omega^2\tau^2)} \right. \\ &\times \left. \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \right]. \end{aligned} \quad (84)$$

Now, if $\alpha=0$, the above equation becomes:

$$\frac{\delta_M}{A E_0^2} = \frac{1}{2} \left[1 \pm \frac{1}{(1+4\omega^2\tau^2/9)^{1/2}} \right]. \quad (85)$$

If we write τ instead of $\tau/3$ in Eq. (85), it is in agreement with the equation obtained by O'Konski and Haltner.

One can also calculate the retardation of the electric birefringence $(\varphi + \psi)$ relative to the electric field. By making use of Eqs. (64) and (66) and from the relationship $\beta=1/\alpha$,

$$\tan(\varphi + \psi) = 2\omega\tau \frac{2+5\alpha+2\omega^2\tau^2}{6(1+\alpha)+(3-2\alpha)2\omega^2\tau^2}. \quad (86)$$

This is the relationship between the retardation and the frequency.

For the special case $\alpha=0$, Eq. (86) becomes

$$\tan(\varphi + \psi) = \frac{2\omega\tau}{3}. \quad (87)$$

If we write τ instead of $\tau/3$ the above equation is in agreement with the equation obtained by O'Konski and Haltner.

§ 9. Comparison with Experiment

O'Konski and Haltner made investigations of electric birefringence in dilute solutions of TMV in alternating fields. One may now compare their results with the above theory. i) The relationship between phase angle and frequency.

The circles in Fig. 3 show the experimental relationship between phase angle and frequency as found by O'Konski and Haltner. The concentration of TMV is 0.50 g/l and pH is 7.0. The three curves represent Eq. (86). The curves 1, 2 and 3 correspond to $\alpha=0$, 0.1 and 1.0, respectively. The value of τ is taken as 1.5×10^{-3} sec, which is three times greater than the value 0.5×10^{-3} sec taken by O'Konski and Haltner. The theoretical curves do not show much difference for values of α between zero and unity.

ii) The relationship between extreme values of δ_M and frequency.

Fig. 4 shows the experimental values of δ_M

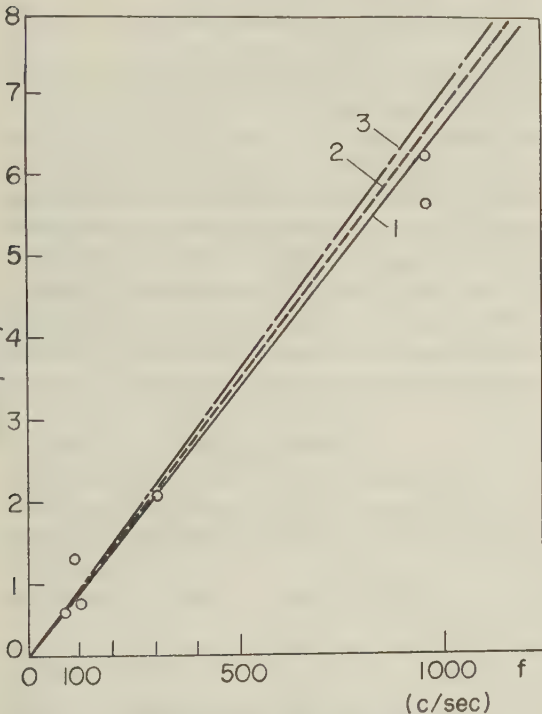


Fig. 3. Phase angle vs. frequency.

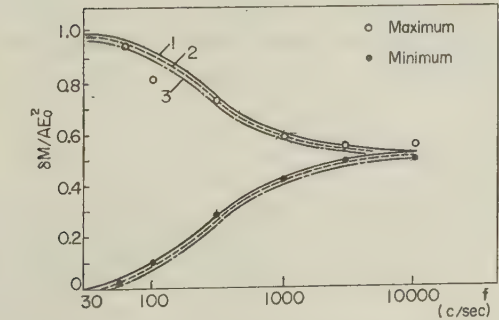


Fig. 4. Maximum and minimum values of δ_M vs. frequency.

obtained by O'Konski and Haltner. The concentration of TMV is 0.50 g/l and pH is 7.0. The curves show the calculated values from Eq. (84). The curves 1, 2 and 3 correspond to $\alpha=0$, 0.01 and 0.1, respectively. The maximum and minimum values decrease with the increasing α and both curves tend to deviate from symmetry. However, they are almost symmetric for values of α less than 0.1, and there is little difference between the curves for $\alpha=0$ and $\alpha=0.1$.

If it is assumed that the permanent dipole moment μ is zero, α becomes zero, but as seen in the case of i) and ii) the theoretical curves are in agreement with experimental values even when α is assumed to be 0.01 or 0.1. Therefore, one cannot draw the conclusion that α is zero.

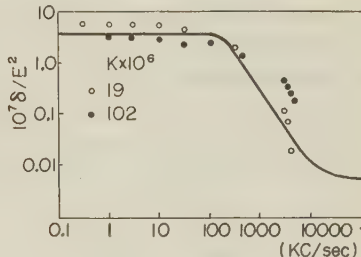


Fig. 5. Birefringence vs. frequency.

iii) The relationship between the mean value δ_0 and frequency.

Fig. 5 shows the experimental values obtained by O'Konski and Haltner. κ is the conductivity of the solution and the concentration of TMV is 0.50 g/l and pH is 7.0. The solid curve shows the calculated values from Eq. (82). The values of α and τ are chosen so that the theoretical values, that is $\alpha=1000$ and $\tau=0.5 \times 10^{-6}$ sec. This value of α is quite large compared with the value in the case of i) and ii). In this case the frequency reaches 10,000 kc while in the cases of i) and ii) the frequencies do not exceed 1 kc and 10 kc, respectively. Further it may be considered that the electrical anisotropy factor, $(g_{e1}-g_{e2})$, decreases with the increase of frequency. Thus, it is quite reasonable that α takes large value in this case.

iv) Birefringence in a rapidly reversed electric field.

O'Konski and Haltner decided that the permanent dipole moment does not contribute to the electrical orientation of TMV by means

of reversing square pulse experiment. Fig. 6 shows the behavior of electric birefringence when the electric field is rapidly reversed.

Now, if one considers, as in Fig. 7 that there is a duration Δt , in which the electric field is zero between the negative and positive square wave field, then the birefringence will

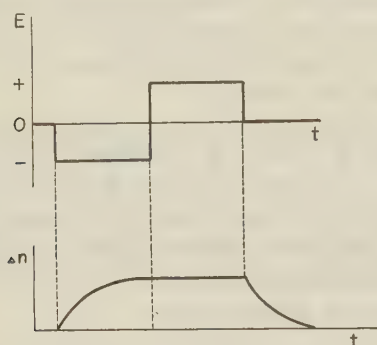


Fig. 6a. Electric field strength of the reversing square pulse vs. time.

Fig. 6b. Birefringence vs. time.

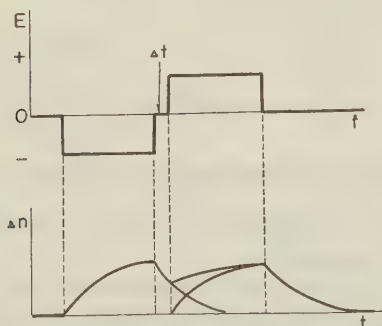


Fig. 7a. Electric field strength of the reversing square pulse vs. time.

Fig. 7b. Birefringence vs. time.

be a superposition of a decay curve and a build-up curve. Consequently it may be possible that the birefringence does not change when Δt tends to zero.

v) The value of an intrinsic Kerr constant.

One may write the birefringence Δn for a

static field E as follows:

$$\Delta n = K n E^2. \quad (88)$$

Then, K is almost independent of the wave length λ_0 . If the concentration is denoted by c , the quantity

$$[K] = \lim_{c \rightarrow 0} K/c \quad (89)$$

is called intrinsic Kerr constant. From Eqs. (80) and (81) the following equation is easily obtained

$$[K] = \frac{2\pi}{15} \cdot \frac{V}{kT} (g_1 - g_2)(g_{e1} - g_{e2})(1 + \alpha). \quad (90)$$

When α is zero, the above equation reduces to

$$[K] = \frac{2\pi}{15} \cdot \frac{v}{kT} (g_1 - g_2)(g_{e1} - g_{e2}). \quad (91)$$

O'Konski and Haltner calculated the value of $[K]$ from Eq. (91) and found that the experimental value is fifty times greater than the calculated one. However, it may be possible to explain this discrepancy, if one considers the effect of the surface polarization. In this case g_i and g_{ei} will be replaced by $g_i + r g_i'$ and $g_{ei} + r g_{ei}'$, respectively, where r is the ratio of the surface area to the volume of the particle. Thus, it is expected that the intrinsic Kerr constant increases.

References

- 1) F. C. Bawden, N. W. Pirie, J. D. Bernel and I. Fankuchen: *Nature* **138** (1936) 1051.
- 2) M. A. Lauffer: *J. Amer. Chem. Soc.* **61** (1939) 2412.
- 3) C. T. O'Konski and B. H. Zimm: *Science* **111** (1950) 113.
- 4) H. Benoit: *Ann. Physique* 12^e Serie **6** (1951) 561.
- 5) C. T. O'Konski and A. J. Haltner: *J. Amer. Chem. Soc.* **78** (1956) 3604.
- 6) C. T. O'Konski and A. J. Haltner: *J. Amer. Chem. Soc.* **79** (1957) 5634.
- 7) A. Peterlin and H. A. Stuart: *Z. Phys.* **112** (1939) 1, 129.

Notes on the Theory of Meissner Effect*

By Masayuki ASAMI and Fumihiko TAKANO

Department of Physics, Tokyo University of Education

(Received December 5, 1959)

The gauge invariance of B.C.S. explanation of the Meissner effect is guaranteed by the inclusion of the collective excitations, as shown by Anderson and Yosida. In this case, however, the current, which can be neglected in B.C.S. calculation, might become to make a finite contribution to the Meissner effect. It is shown that this is actually the case in a system of normal electrons with Coulomb interactions. The situation in superconductors does not seem to differ essentially from that of normal electrons with this respect. This conclusion means that the gauge invariant theory of the Meissner effect cannot be said to be complete unless this difficulty is solved.

Moreover, the canonical transformation leading to the B.C.S. model adds some terms to the current operator. The magnitude of these terms is estimated, and is shown to make a numerically small but finite contribution to the Meissner effect also.

§ 1. Introduction

Since Bardeen, Cooper and Schrieffer¹⁾ succeeded to explain the Meissner effect in the superconductor, many authors discussed the problem of its gauge invariance. Anderson²⁾ and Yosida³⁾ pointed out that the longitudinal collective excitation in the superconductor guaranteed the gauge invariance of the Meissner effect and this excitation was nothing but the plasma excitation. This fact can be considered as follows:

The problem of gauge invariance is equivalent to examine whether the equation of continuity

$$[H, \rho(\mathbf{p})] = \frac{\hbar}{e} \mathbf{p} \cdot \mathbf{j}(\mathbf{p}) \quad (1.1)$$

holds or not. Here, $\rho(\mathbf{p})$ and $\mathbf{j}(\mathbf{p})$ are the Fourier components of density and current operators, respectively, and H is the Hamiltonian of the system. It is essential for the problem of the gauge invariance that H is not the starting Hamiltonian but the "reduced" or "model" Hamiltonian of which eigen

functions can be calculated rigorously.

The fact that the calculation of B.C.S. is not gauge invariant can be easily shown by taking the Bogoliubov's⁴⁾ Hamiltonian for which the B.C.S. functions are exact eigenfunctions,

$$H_0 = \sum_{\mathbf{k}} E_{\mathbf{k}} (\alpha_{\mathbf{k}0}^\dagger \alpha_{\mathbf{k}0} + \alpha_{\mathbf{k}1}^\dagger \alpha_{\mathbf{k}1}) \quad (1.2)$$

where

$$\begin{aligned} \alpha_{\mathbf{k}0} &= u_{\mathbf{k}} a_{\mathbf{k}\uparrow} - v_{\mathbf{k}} a_{-\mathbf{k}\downarrow}^\dagger, \\ \alpha_{\mathbf{k}1} &= u_{\mathbf{k}} a_{-\mathbf{k}\downarrow} + v_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger, \\ E_{\mathbf{k}} &= (\varepsilon_{\mathbf{k}}^2 + \varepsilon_0^2)^{1/2}, \end{aligned} \quad (1.3)$$

and $\varepsilon_{\mathbf{k}}$ is the kinetic energy of an electron measured from the Fermi surface, and ε_0 is the energy gap. Substituting Eq. (1.3) into Eq. (1.2), and using the relation,

$$\begin{aligned} u_{\mathbf{k}}^2 &= \frac{1}{2} \left[1 + \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right] \\ v_{\mathbf{k}}^2 &= \frac{1}{2} \left[1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right], \end{aligned} \quad (1.4)$$

H_0 becomes

$$H_0 = \sum_{\mathbf{k}, s} \varepsilon_{\mathbf{k}} a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s} - \varepsilon_0 \sum_{\mathbf{k}} (a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger + a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}) = K + V'.$$

In $[H_0, \rho(\mathbf{p})]$, $[K, \rho(\mathbf{p})]$ is nothing but $\hbar/e \cdot \mathbf{p} \cdot \mathbf{j}(\mathbf{p})$, but $[V', \rho(\mathbf{p})]$ remains finite in the limit of $p \rightarrow 0$ in contrast with $[K, \rho(\mathbf{p})]$ which vanishes in this limit so that V' can not be neglected in $[H_0, \rho(\mathbf{p})]$. Thus, we can say that the calculation of B.C.S. is not gauge invariant.

* Parts of the paper are based on a thesis submitted by Dr. Asami in partial fulfillment of the requirements for a D. S. degree in Physics, Tokyo University of Education, 1959.

Anderson's assertion that the inclusion of the collective excitations guarantee the gauge invariance can be checked very easily. The inclusion of the collective excitation means that the "model" Hamiltonian to be used in Eq. (1.1) is of the form taken by Yosida³⁾,

$$\mathcal{H}_0 = \sum_{p, k} W_p(\mathbf{k}) \beta_p^+(\mathbf{k}) \beta_p(\mathbf{k}) + \sum_p \sum_{k, k'} \{ A_p(\mathbf{k}, \mathbf{k}') \beta_p^+(\mathbf{k}) \beta_p(\mathbf{k}') + \frac{1}{2} B_p(\mathbf{k}, \mathbf{k}') [\beta_p^+(\mathbf{k}) \beta_{-p}^+(\mathbf{k}') + \beta_p(\mathbf{k}) \beta_{-p}(\mathbf{k}')] \} , \quad (1.5)$$

where

$$\beta_p^+(\mathbf{k}) = \alpha_{k+p0}^+ \alpha_{k1}^+ \quad (1.6)$$

and

$$\beta_p(\mathbf{k}) = \alpha_{k1} \alpha_{k+p0}$$

are treated as Bose operators

$$[\beta_p(\mathbf{k}), \beta_{p'}^+(\mathbf{k}')] = \delta_{p, p'} \delta_{\mathbf{k}, \mathbf{k}'} , \quad (1.7)$$

and $W_p = E_k + E_{k+p}$ and $A_p(\mathbf{k}, \mathbf{k}')$, $B_p(\mathbf{k}, \mathbf{k}')$ are given in Yosida's paper.

$\rho(\mathbf{p})$ and $\mathbf{j}(\mathbf{p})$ can be written in terms of α^+ , α as

$$\begin{aligned} \rho(\mathbf{p}) = & \sum_k (\mathcal{U}_k v_{k+p} + v_k \mathcal{U}_{k+p}) (\alpha_{k+p0}^+ \alpha_{k1}^+ + \alpha_{k+p1} \alpha_{k0}) \\ & + \sum_k (\mathcal{U}_k \mathcal{U}_{k+p} - v_k v_{k+p}) (\alpha_{k+p0}^+ \alpha_{k0} + \alpha_{k1}^+ \alpha_{k+p1}) , \end{aligned} \quad (1.8a)$$

$$\begin{aligned} \mathbf{j}(\mathbf{p}) = & \frac{e\hbar}{m} \sum_k \left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) (\mathcal{U}_{k+p} v_k - v_{k+p} \mathcal{U}_k) (\alpha_{k+p0}^+ \alpha_{k1}^+ - \alpha_{k+p1} \alpha_{k0}) \\ & + \frac{e\hbar}{m} \sum_k \left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) (\mathcal{U}_{k+p} \mathcal{U}_k + v_{k+p} v_k) (\alpha_{k+p0}^+ \alpha_{k0} - \alpha_{k1}^+ \alpha_{k+p1}) , \end{aligned} \quad (1.8b)$$

which is expressed in terms of β^+ , β as

$$\begin{aligned} \rho(\mathbf{p}) &= \rho_0(\mathbf{p}) + \rho_1(\mathbf{p}) \\ \mathbf{j}(\mathbf{p}) &= \mathbf{j}_0(\mathbf{p}) + \mathbf{j}_1(\mathbf{p}) \end{aligned} \quad (1.9)$$

where ρ_0 , $\mathbf{j}_0$ are linear in β^+ or β and ρ_1 , $\mathbf{j}_1$ are remaining terms,

$$\begin{aligned} \rho_0(\mathbf{p}) &= \sum_k (\mathcal{U}_k v_{k+p} + v_k \mathcal{U}_{k+p}) (\beta_p^+(\mathbf{k}) + \beta_{-p}(\mathbf{k} + \mathbf{p})) \\ \mathbf{j}_0(\mathbf{p}) &= \frac{e\hbar}{m} \sum_k \left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) (\mathcal{U}_{k+p} v_k - v_{k+p} \mathcal{U}_k) (\beta_p^+(\mathbf{k}) - \beta_{-p}(\mathbf{k} + \mathbf{p})) . \end{aligned} \quad (1.10)$$

Then it is straightforward to show that the equation of continuity (1.1) holds for $\mathcal{H}_0$, Eq. (1.5) and ρ_0 , $\mathbf{j}_0$, Eq. (1.10),

$$[\mathcal{H}_0, \rho_0(\mathbf{p})] = \frac{\hbar}{e} \mathbf{p} \cdot \mathbf{j}_0(\mathbf{p}) \quad (1.11)$$

in the limit of $p \rightarrow 0$, irrespective whether the Coulomb interactions are taken into account or not. The proof will be given in the Appendix. Thus, the gauge invariance can be guaranteed by the inclusion of the collective excitation.

Here the question arises whether $\mathbf{j}_1$ can be neglected or not. In Wentzel's formalism⁵⁾, we can write down this question in a following way. In the presence of the magnetic field, the Hamiltonian and the current of the system can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}_A , \quad (1.12)$$

$$\mathbf{J}(\mathbf{p}) = \mathbf{j}(\mathbf{p}) + \mathbf{j}_A(\mathbf{p}) , \quad (1.13)$$

where $\mathcal{H}_0$ is given by Eq. (1.5), $\mathbf{j}(\mathbf{p})$ by Eq. (1.9) and $\mathcal{H}_A = -1/c\Omega \cdot \sum_{\mathbf{p}} \mathbf{j}(-\mathbf{p}) \cdot \mathbf{A}_{\mathbf{p}}$ and $\mathbf{j}_A(\mathbf{p}) = -e^2/mc\Omega \cdot \sum_{\mathbf{p}'} \mathbf{A}_{\mathbf{p}'} \rho_{\mathbf{p}-\mathbf{p}'}$. We eliminate $\mathcal{H}_A$ with the transformation K_A , $[\mathcal{H}_0, K_A] + \mathcal{H}_A = 0$. Then, Eqs. (1.12) and (1.13) become

$$\begin{aligned}\mathcal{H}_1 &= \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}'_A + O(A^2), \\ \mathbf{J}_1(\mathbf{p}) &= \mathbf{j}(\mathbf{p}) + \mathbf{j}'_A(\mathbf{p}) + \mathbf{j}_A(\mathbf{p}) + O(A^2),\end{aligned}$$

where

$$\mathbf{j}'_A(\mathbf{p}) = [\mathbf{j}(\mathbf{p}), K_A] = [\mathbf{j}_0(\mathbf{p}), K_A] + [\mathbf{j}_1(\mathbf{p}), K_A] = \mathbf{j}'_{0A}(\mathbf{p}) + \mathbf{j}'_{1A}(\mathbf{p}). \tag{1.14}$$

The perturbational Hamiltonian $\mathcal{H}'$ is assumed to be so small that $\mathcal{H}'_A$ may be neglected. Then, we can take the expectation value of $\mathbf{J}_1(\mathbf{p})$ with the ground state of $\mathcal{H}_0$. The result is

$$\langle \mathbf{J}_1(\mathbf{p}) \rangle_0 = \langle \mathbf{j}'_A(\mathbf{p}) \rangle_0 + \langle \mathbf{j}_A(\mathbf{p}) \rangle_0 + O(A^2) = \langle \mathbf{j}'_{0A}(\mathbf{p}) \rangle_0 + \langle \mathbf{j}'_{1A}(\mathbf{p}) \rangle_0 + \langle \mathbf{j}_A(\mathbf{p}) \rangle_0 + O(A^2).$$

The assertion of Anderson proved by Yosida and by the above argument is that $\langle \mathbf{j}'_{0A}(\mathbf{p}) \rangle_0 + \langle \mathbf{j}_A(\mathbf{p}) \rangle_0$ becomes $-ne^2/mc \cdot (\delta_{\mu\nu} - p_\mu p_\nu / p^2) A_\nu(\mathbf{p})$ in the limit $p \rightarrow 0$, giving the gauge invariant Meissner effect. The above question is the effect of $\langle \mathbf{j}'_{1A}(\mathbf{p}) \rangle_0$. The inclusion of this term leads to the result not gauge invariant, of course, but it is necessary for the consistent theory to show the smallness of this term. It is the purpose of this note to investigate this question. Moreover, the canonical transformation leading to the Hamiltonian (1.12) leads to the additional current $\mathbf{j}_g$, the effect of which must be examined. We shall examine the effect of $\mathbf{j}_1$ in § 2, and $\mathbf{j}_g$ in § 3. The result is not as was expected; the effect of these current does not appear as small compared with $\mathbf{j}_0$, but make finite contributions to the Meissner effect. Thus, the problem of the gauge invariance must be considered not to be solved completely.

§ 2. Estimation of Contribution from $\mathbf{j}_1$ to Meissner Effect

$\mathbf{j}_1(\mathbf{p})$ is given by the second term of Eq. (1.8b) and vanishes when operated to the ground state of B.C.S. or Bogoliubov's Hamiltonian (1.2), but does not vanish when operated to that of the Hamiltonian (1.5). No one investigated this current, however. The purpose of this section is to estimate the contribution of this current to the Meissner effect, and we want to show that this current is not small compared with $\mathbf{j}_0$, and can not be neglected.

First, it is necessary to write down $\mathbf{j}_1$ in terms of β^+ and β . This can be done by the technique which Dyson⁶⁾ used in the discussion of the interactions between spin waves. The result is

$$\mathbf{j}_1(\mathbf{p}) = \frac{e\hbar}{m} \sum_{\mathbf{k}} \left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) (u_{\mathbf{k}} u_{\mathbf{k}+\mathbf{p}} + v_{\mathbf{k}} v_{\mathbf{k}+\mathbf{p}}) \sum_{p_1} [\beta_{\mathbf{p}+\mathbf{p}_1}^+ (\mathbf{k}-\mathbf{p}_1) \beta_{\mathbf{p}_1} (\mathbf{k}-\mathbf{p}_1) - \beta_{\mathbf{p}+\mathbf{p}_1}^+ (\mathbf{k}) \beta_{\mathbf{p}_1} (\mathbf{k}+\mathbf{p})]. \tag{2.1}$$

When Dyson's technique is used, $\mathbf{j}_1(\mathbf{p})$ contains terms of third power of β^+ and β , which is neglected in this note.

Next task is to get the matrix elements of $\mathbf{j}_1(\mathbf{p})$ between the eigenstates of the Hamiltonian $\mathcal{H}_0$, (1.5). To do so, it is necessary to express β^+ , β and thus $\mathbf{j}_1(\mathbf{p})$ in terms of the normal coordinate of $\mathcal{H}_0$. While the normal coordinate of the collective excitation was already obtained by Yosida, those of the individual excitations are difficult to calculate. So, we want to investigate the case of normal electrons with Coulomb interactions. The situation of this latter case is quite similar to that in the superconductor. Moreover, in the limit of $p \rightarrow 0$, the coefficient of $\beta^+ \beta$ in (2.1) does not include the energy gap ($u^2 + v^2 = 1$). We can expect, therefore, that the conclusion about $\mathbf{j}_1(\mathbf{p})$ in the normal case does not change essentially in the superconductor.

The normal electrons with Coulomb interactions were discussed by Gell-Mann, Brueckner and Sawada⁷⁾ and others. We take the Sawada's Hamiltonian,

$$H = \sum_{p,k} \omega_p(k) \beta_{p^+}(k) \beta_p(k) + \sum_p \lambda_p \sum_{k,k'} \left\{ \beta_{p^+}(k) \beta_p(k') + \frac{1}{2} (\beta_{p^+}(k) \beta_{-p}^+(k') + \beta_p(k) \beta_{-p}^-(k')) \right\} \quad (2.2)$$

where

$$\lambda_p = \frac{4\pi e^2}{p^2 \Omega} \quad (2.3)$$

$$\beta_{p^+}(k) = a_{k+p}^+ b_{k^+}, \quad \beta_p(k) = b_k a_{k+p}, \quad \left(\begin{array}{l} |k| < k_0 \\ |k+p| > k_0 \end{array} \right). \quad (2.4)$$

a_k and b_k are the operators for excited electrons outside the Fermi sphere (radius k_0), and the holes inside, respectively.

The current can be divided into j_0 and j_1 as in the discussion in § 1, and the equation of continuity $[H, \rho_0] - \hbar/e \cdot p \cdot j_0(p)$ holds (the second term of (2.2) commutes with ρ_0). $\langle j_{0,1}(p) \rangle_0$ defined in a similar way as in Eq. (1.14), is completely equal to the value corresponding to free electrons (no Coulomb interactions), as shown by Wentzel⁸⁾.

The current $j_1(p)$ is of the form

$$j_1(p) = \frac{e\hbar}{m} \sum_k \left(k + \frac{1}{2} p \right) \sum_{p_1} \{ \beta_{p+p_1}^+(k-p_1) \beta_{p_1}(k-p_1) - \beta_{p+p_1}^+(k) \beta_{p_1}(k+p) \} \quad (2.5)$$

which coincides with Eq. (2.1) in the limit of $p \rightarrow 0$. The normal coordinates U^+ and U of H , (2.2), were obtained by Sawada, and the transformation matrix between β^+ , β and U^+ , U is written in a following way

$$\begin{aligned} \beta_{p^+}(k) &= \sum_{k'} [c_p(k', k) U_{p^+}(k') - d_p(k', k) U_{-p}(k')] , \\ \beta_p(k) &= \sum_{k'} [c_p^*(k', k) U_p(k') - d_p^*(k', k) U_{-p}^+(k')] . \end{aligned} \quad (2.6)$$

In this summation we include the plasma mode which will be written as U_{p^+} , U_p and $c_p(0, k)$ and $d_p(0, k)$ etc. c and d are given as follows⁹⁾:

For individual modes:

$$\begin{aligned} c_p(k, k') &= \delta_{k,k'} + \frac{\lambda_p}{1 - \Delta_p(k')} \frac{1}{\omega_p(k') - \omega_p(k) - i\alpha} \\ d_p(k, k') &= \frac{\lambda_p}{1 - \Delta_p^*(k')} \frac{1}{\omega_p(k') + \omega_p(k)} \end{aligned} \quad (2.7)$$

where

$$\Delta_p(k) = \lambda_p \sum_{k_1}' \left\{ \frac{1}{\omega_p(k) - \omega_p(k_1) - i\alpha} - \frac{1}{\omega_p(k) + \omega_p(k_1)} \right\} \quad (2.8)$$

α is a positive number which is taken as arbitrarily small. For plasma mode:

$$\begin{aligned} c_p(0, k) &= N_p \frac{1}{\Omega_p - \omega_p(k)} \\ d_p(0, k) &= N_p \frac{1}{\Omega_p + \omega_p(k)} \end{aligned} \quad (2.9)$$

where

$$N_p^2 \sum_k' \left\{ \frac{1}{(\Omega_p - \omega_p(k))^2} - \frac{1}{(\Omega_p + \omega_p(k))^2} \right\} = 1 \quad (2.10)$$

and Ω_p is the plasma frequency which satisfies the following dispersion relation,

$$\lambda_p \sum_k' \left\{ \frac{1}{\Omega_p - \omega_p(k)} - \frac{1}{\Omega_p + \omega_p(k)} \right\} = 1. \quad (2.11)$$

In all the above equations, $\sum'_k$ means a sum over k with the restriction $|k| < k_0$, $|k+p| > k_0$. Of course, the Hamiltonian H , (2.2), is diagonalized by these U^+ , U ,

$$H = \sum_p \left[\sum_k \omega_p(k) U_{p^+}(k) U_p(k) + \Omega_p U_{p^+} U_p \right] + \text{const.}$$

Now, let us compute $\langle j_{1A}(p) \rangle_0$ in the limit of $p \rightarrow 0$. This quantity can be written as

$$\begin{aligned} \langle j_{1A}(p) \rangle_0 &= \frac{1}{c\Omega} \sum_s \langle 0 | j_1(p) | s \rangle \langle s | j(-p) \cdot A_p | 0 \rangle \\ &\quad - \langle 0 | j(-p) \cdot A_p | s \rangle \langle s | j_1(p) | 0 \rangle \left[\frac{1}{E_s - E_0} \right]. \end{aligned} \quad (2.12)$$

The cross terms of j_0 and j_1 vanish, because j_1 is quadratic in U^+ and U , while j_0 is linear, so that it is sufficient to evaluate matrix elements of $j_1(p)$ and to sum over s in the limit of $p \rightarrow 0$.

Using Eq. (2.6), the matrix elements of $j_1(p)$ can be calculated as

$$\begin{aligned} j_1(p) &= \frac{e\hbar}{m} \sum_k \left(k + \frac{1}{2} p \right) \sum_{k', k''} \sum_{p_1} c_{p+p_1}(k', k) d_{p_1}^*(k'', k+p) \\ &\quad - c_{p+p_1}(k', k-p_1) d_{p_1}^*(k'', k-p_1) \} U_{p+p_1}^+(k') U_{-p_1}^+(k'') | 0 \rangle. \end{aligned} \quad (2.13)$$

We shall evaluate the above expression in three cases, separately.

(a) $k', k'' = 0$: $|s\rangle$ is the state in which two plasmons are excited. In this case the coefficient of $U_{p+p_1}^+ U_{-p_1}^+ | 0 \rangle$ in the right hand side of Eq. (2.13) becomes

$$\begin{aligned} & - \frac{e\hbar}{m} N_{p+p_1} N_{p_1} \sum_k \left[\left(k + p_1 + \frac{1}{2} p \right) \left\{ \frac{1}{\Omega_{p+p_1} - \omega_{p+p}(k)} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k)} - \frac{1}{\Omega_{p_1} - \omega_{p_1}(k)} \frac{1}{\Omega_{p+p_1} + \omega_{p+p_1}(k)} \right\} \right. \\ & \quad \left. - \left(k + \frac{1}{2} p \right) \left\{ \frac{1}{\Omega_{p+p_1} - \omega_{p+p_1}(k)} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k+p)} - \frac{1}{\Omega_{p_1} - \omega_{p_1}(k+p)} \frac{1}{\Omega_{p+p_1} + \omega_{p+p_1}(k)} \right\} \right] \end{aligned}$$

This expression vanishes in the limit of $p \rightarrow 0$, so that the contribution to Eq. (2.12) also vanishes (the energy denominator does not vanish).

(b) $k' \neq 0, k'' = 0$: $|s\rangle$ is the state in which one plasmon and one individual excitation are excited. The coefficient of $U_{p+p_1}^+(k') \cdot U_{-p_1}^+ | 0 \rangle$ in Eq. (2.13) becomes

$$\begin{aligned} & - \frac{e\hbar}{m} \left\{ \left(k' + p_1 + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k')} - \left(k' + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k' + p)} \right\} \\ & - \frac{e\hbar}{m} \sum_k \left\{ \left(\left(k + p_1 + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k')} - \left(k + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} + \omega_{p_1}(k+p)} \right) \right. \\ & \quad \times \frac{\lambda_{p+p_1}}{1 - \Delta_{p+p_1}(k')} \frac{1}{\omega_{p+p_1}(k') - \omega_{p+p_1}(k) - i\alpha} \\ & \quad \left. - \left(\left(k + p_1 + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} - \omega_{p_1}(k)} - \left(k + \frac{1}{2} p \right) N_{p_1} \frac{1}{\Omega_{p_1} - \omega_{p_1}(k+p)} \right) \right. \\ & \quad \left. \times \frac{\lambda_{p+p_1}}{1 - \Delta_{p+p_1}(k')} \frac{1}{\omega_{p+p_1}(k') + \omega_{p+p_1}(k)} \right\}. \end{aligned}$$

Since this has no singularity at $p=0$, we can put $p=0$ in this expression, which becomes

$$\begin{aligned} & - \frac{e\hbar}{m} N_{p_1} p_1 \left\{ \frac{1}{\Omega_{p_1} + \omega_{p_1}(k')} + \frac{\lambda_{p_1}}{1 - \Delta_{p_1}(k')} \sum_k \left(\frac{1}{\Omega_{p_1} + \omega_{p_1}(k)} \frac{1}{\omega_{1p}(k') - \omega_{p_1}(k) - i\alpha} \right. \right. \\ & \quad \left. \left. - \frac{1}{\Omega_{p_1} - \omega_{p_1}(k)} \frac{1}{\omega_{p_1}(k') + \omega_{p_1}(k)} \right) \right\} \\ & = - \frac{e\hbar}{m} N_{p_1} p_1 \frac{1}{\Omega_{p_1} + \omega_{p_1}(k')} \frac{2}{1 - \Delta_{p_1}(k')}, \end{aligned}$$

where we used the relations (2.8) and (2.11).

The corresponding energy denominator in Eq. (2.12) remains finite even if $p=0$, so that the contribution to Eq. (2.12) from this term never vanishes.

(c) $k', k'' \neq 0$: In this case the calculation is similar to that in case (b). The coefficient of $U_{p+p_1}^+(k')U_{-p_1}^+(k'')|0\rangle$ in Eq. (2.13) becomes in the limit of $p \rightarrow 0$,

$$-\frac{e\hbar}{m}p_1\frac{\lambda_{p_1}}{\omega_{p_1}(k')+\omega_{p_1}(k'')}\left(\frac{1}{1-\Delta_{p_1}(k')}-\frac{1}{1-\Delta_{p_2}(k'')}\right)$$

which is finite also.

Moreover, the various contributions to Eq. (2.12) are all positive and any cancellation never occurs. The above calculation is in the case of the normal electrons. In this case, the contribution of j_0 just cancels out the London current leaving the terms quadratic of p (Landau diamagnetism) as was shown by Wentzel⁹⁾. The fact, that the contribution of j_1 does not vanish in the limit of $p \rightarrow 0$ (Meissner effect?), only means that the Hamiltonian (2.2) is not appropriate for the starting Hamiltonian to calculate the current, and that to take into account of j_1 , another consistent approximation must be used.

In the superconductor, the contribution of j_0 essentially differs from that of normal electrons, but there is no reason to expect that the above conclusion is essentially changed, because in the above calculation, the energy gap does not make any essential role. In fact, the similar conclusion is reached if we use the Bohm-Pines treatment in the case of superconductor. Thus, it is not valid that the current j_1 is ignored at all even in the superconductor.

§ 3. Estimation of the Contribution from j_g

To find the explicit form of j_g , it is necessary to find the canonical transformation which lead to the energy gap model, Eq. (1.2), of B.C.S.. Since neither the Coulomb interaction between electrons nor the renormalization technique is important in this problem, we follow the simplest treatment of Bogoliubov⁴⁾. Thus, the starting Hamiltonian is taken as

$$H = \sum_k \varepsilon_k a_{ks}^+ a_{ks} + \sum_q \omega_q b_q^+ b_q + \sum_g g_q a_{ks}^+ a_{k+q,s} (b_q^+ + b_{-q}).$$

Introducing the α particle defined by Eq. (1.3), this Hamiltonian can be written as

$$H = U + H_0 + H_1 + H_2 + H_3,$$

where U is a constant term, H_0 is the self-energies of α particles and phonons, H_1 and H_2 the electron-phonon interactions of the forms $\alpha^\dagger \alpha^\dagger (b^+ + b)$ and $\alpha^\dagger \alpha (b^+ + b)$, respectively, and H_3 is the "dangerous" term containing $\alpha_{k0}^+ \alpha_{k1}^+$ and $\alpha_{k1} \alpha_{k0}$. The perturbational canonical transformation which eliminated H_1 and H_2 is given by $K = \exp(S_1 + S_2)$, where $[H_0, S_1] + H_1 = 0$, $[H_0, S_2] + H_2 = 0$. The explicit expression of S_1 and S_2 are given by,

$$S_1 = \sum_{k, k', q} (A_1(k, k', q) b_{-q}^+ + B_1(k, k', q) b_q) \alpha_{k0}^+ \alpha_{k1}^+ - c.c. \quad (3.2a)$$

$$S_2 = \sum_{k, k', q} A_2(k, k', q) (\alpha_{k0}^+ \alpha_{k'0} b_{-q}^+ - \alpha_{k'1}^+ \alpha_{k1} b_q) - c.c., \quad (3.2b)$$

where we write

$$\left. \begin{aligned} A_1(k, k', q) \} &= -g_q \frac{M(k, k')}{\varepsilon_k + \varepsilon_{k'} \pm \omega_q} \delta_{k, k'+q} \\ B_1(k, k', q) \} \\ A_2(k, k', q) &= -g_q \frac{L(k, k')}{\varepsilon_k - \varepsilon_{k'} + \omega_q} \delta_{k, k'+q} \end{aligned} \right\} \quad (3.3)$$

and

$$\begin{aligned} M(\mathbf{k}, \mathbf{k}') &= u_{\mathbf{k}} v_{\mathbf{k}'} + v_{\mathbf{k}} v_{\mathbf{k}'} , \\ L(\mathbf{k}, \mathbf{k}') &= u_{\mathbf{k}} u_{\mathbf{k}'} - v_{\mathbf{k}} v_{\mathbf{k}'} . \end{aligned} \quad (3.4)$$

$u_{\mathbf{k}}, v_{\mathbf{k}}$ are determined from the condition that the "dangerous" terms $\alpha^+ \alpha^+$ in the transformed Hamiltonian should vanish, and is given by Eq. (1.4) in the B.C.S. approximation. The diagonal part of the transformed Hamiltonian is the Bogoliubov Hamiltonian, Eq. (1.2).

The transformation K adds some terms to the current operator,

$$\mathbf{j}_g = [\mathbf{j}, S_1 + S_2] + \frac{1}{2} [[\mathbf{j}, S_1 + S_2], S_1 + S_2] + \dots$$

where $\mathbf{j}$ is given by Eq. (1.8b), and S_1, S_2 by Eqs. (3.2a, b). Since we want to calculate the expectation value of the current in the ground state, the only necessary term is such that $\langle 0 | \mathbf{j}_g | 0 \rangle$ does not vanish. Such a term can be divided into three terms,

$$\begin{aligned} \mathbf{j}_g^1(\mathbf{p}) &= \frac{e\hbar}{m} \sum_{\mathbf{k}} \left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) M'(\mathbf{k}, \mathbf{k} + \mathbf{p}) \\ &\quad \cdot [A_1(\mathbf{k}, \mathbf{k} + \mathbf{p}, \mathbf{p}) - B_1(\mathbf{k}, \mathbf{k} + \mathbf{p}, \mathbf{p})] (b_{-\mathbf{p}} - b_{\mathbf{p}}^+) \end{aligned} \quad (3.5a)$$

$$\begin{aligned} \mathbf{j}_g^2(\mathbf{p}) &= \frac{e\hbar}{m} \sum_{\mathbf{k}, \mathbf{k}'} \left[\left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) L'(\mathbf{k}, \mathbf{k} + \mathbf{p}) A_1(\mathbf{k} + \mathbf{p}, \mathbf{k}' + \mathbf{p}, \mathbf{k} - \mathbf{k}') \right. \\ &\quad \left. - \left(\mathbf{k}' - \frac{1}{2} \mathbf{p} \right) L'(\mathbf{k}', \mathbf{k}' + \mathbf{p}) A_1(\mathbf{k}, \mathbf{k}', \mathbf{k} - \mathbf{k}') \right] \\ &\quad \cdot (b_{-\mathbf{k} + \mathbf{k}'}^+ \alpha_{\mathbf{k}0}^+ \alpha_{\mathbf{k}' + \mathbf{p}1}^+ - b_{\mathbf{k} - \mathbf{k}'} \alpha_{\mathbf{k}1} \alpha_{\mathbf{k}' + \mathbf{p}0}) \end{aligned} \quad (3.5b)$$

$$\begin{aligned} \mathbf{j}_g^3(\mathbf{p}) &= \frac{e\hbar}{m} \sum_{\mathbf{k}, \mathbf{k}'} \left[\left(\mathbf{k} + \frac{1}{2} \mathbf{p} \right) M'(\mathbf{k}, \mathbf{k} + \mathbf{p}) A_2(\mathbf{k} + \mathbf{p}, \mathbf{k}' + \mathbf{p}, \mathbf{k} - \mathbf{k}') \right. \\ &\quad \left. - \left(\mathbf{k}' - \frac{1}{2} \mathbf{p} \right) M'(\mathbf{k}', \mathbf{k}' + \mathbf{p}) A_2(\mathbf{k}, \mathbf{k}', \mathbf{k} - \mathbf{k}') \right] \\ &\quad \cdot (b_{-\mathbf{k} + \mathbf{k}'}^+ \alpha_{\mathbf{k}0}^+ \alpha_{\mathbf{k}' + \mathbf{p}1}^+ - b_{\mathbf{k} - \mathbf{k}'} \alpha_{\mathbf{k}1} \alpha_{\mathbf{k}' + \mathbf{p}0}) \end{aligned} \quad (3.5c)$$

where L' and M' are defined as

$$\begin{aligned} L'(\mathbf{k}, \mathbf{k}') &= u_{\mathbf{k}} u_{\mathbf{k}'} + v_{\mathbf{k}} v_{\mathbf{k}'} , \\ M'(\mathbf{k}, \mathbf{k}') &= u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'} . \end{aligned} \quad (3.6)$$

Here, we neglect the double commutator, since these terms do not contribute anything in the limit of $p \rightarrow 0$. The contributions from the currents (3.5a-c) to expectation value of current can be written in a form like Eq. (2.12). Now, in the limit of $p \rightarrow 0$, the contributions from $\mathbf{j}_g^1, \mathbf{j}_g^3$ vanish because $M'(\mathbf{k}, \mathbf{k} + \mathbf{p}) \rightarrow 0$. In the case of $\mathbf{j}_g^2$, the energy denominator appearing in Eq. (2.12) tends to zero, but the numerator, tends to zero more rapidly.

Thus, the only term we need is $\mathbf{j}_g^2$. The contribution of this current can be calculated and the result is given by, in the limit of $p \rightarrow 0$,

$$2 \left(\frac{e\hbar}{2m} \right)^2 \frac{1}{c\Omega} \sum_{\nu} \sum_{\mathbf{k}, \mathbf{q}} \frac{g^2 q_{\mu} q_{\nu}}{(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k} + \mathbf{q}} + \omega_{\mathbf{q}})^2} \frac{M^2(\mathbf{k}, \mathbf{k} + \mathbf{q})}{(E_{\mathbf{k}} + E_{\mathbf{k} + \mathbf{q}} + \omega_{\mathbf{q}})} A_{\nu}(\mathbf{p}) . \quad (3.7)$$

If we use the B.C.S. approximation in which we put $\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}'}$ or $E_{\mathbf{k}} + E_{\mathbf{k}'} \ll \omega_{\mathbf{q}}$ in the energy denominator, Eq. (3.7) becomes

$$\left(\frac{e\hbar}{2m} \right)^2 \frac{g^2}{c\Omega^2} \sum_{\nu} \sum_{\mathbf{k}, \mathbf{q}} \frac{q_{\mu} q_{\nu}}{\omega_{\mathbf{q}}^2} M^2(\mathbf{k}, \mathbf{k} + \mathbf{q}) A_{\nu}(\mathbf{p}) , \quad (3.7')$$

using the relation $g_{\mathbf{q}} = g(\omega_{\mathbf{q}}/2\Omega)^{1/2}$. In Eq. (3.7'), the characteristic term for superconductors,

which vanishes in the limit of the energy gap $\varepsilon_0 \rightarrow 0$ is the term containing $u_k v_k u_{k+q} v_{k+q}$ in $M^2(k, k+q)$. The order of magnitude of this term is given by

$$\frac{ne^2}{mc} \frac{1}{g^2 N(0)} e^{-1/g^2 N(0)} A(p). \quad (3.8)$$

This is numerically very small for weak interactions, but the higher order terms may contain terms like the above current. The summation of all these terms may contribute a finite quantity to the Meissner effect.

§ 4. Conclusion and Discussions

The B.C.S. explanation of the Meissner effect give excellent agreements with experiments. The problem of its gauge invariance seems to be solved by the inclusion of collective excitations. In this note, however, some doubts are thrown on this viewpoint. The inclusion of collective excitations make the negligible part j_1 of the current in the B.C.S. calculation not negligible. It might be possible that a more accurate "model" Hamiltonian, which has no such difficulties, exists and the Yosida's Hamiltonian, (1.5), is the first approximation of this more accurate one. Even when this is the case, it is still necessary to prove that such a Hamiltonian exists.

In the case of normal electrons, a finite diamagnetic susceptibility may be obtained even taking into account of the above current, if appropriate diagrams of interactions are taken into account¹⁰⁾. It is hoped that this procedure is formulated in Hamiltonian formalism, since then following the Wentzel's treatment⁵⁾ the gauge invariant Meissner effect can be obtained in an analogous way as in the normal electrons.

The discussion in § 3 is not concerned with the problem of gauge invariance. We calculated only the transverse part of the current, but the result, that the current j_q makes a numerically small but finite contribution to the Meissner effect, may have some effects on the calculation of the penetration depth.

The authors wish to express their sincere thanks to Professor M. Toda for his encouragement and helpful discussions.

Appendix. Proof of Eq. (1.11)

Using Eqs. (1.5) and (1.10), $[\mathcal{H}_0, \rho_0(p)]$ can be calculated and the result is

$$[\mathcal{H}_0, \rho_0(p)] = \sum_k \{ W_p(k) M(k, k+p) + \sum_{k'} M(k', k'+p) (A_p(k, k') - B_p(k, k'+p)) \} \cdot (\beta_{p^+}(k) - \beta_{-p}(k+p)). \quad (A.1)$$

A_p and B_p are given in the paper of Yosida³⁾

$$A_p(k, k') = \frac{1}{\Omega} \left[v(k' - k) - \frac{1}{2} (J(k, k') + J(k+p, k'+p)) \right] L(k, k') L(k+p, k'+p) + \frac{1}{\Omega} \left[v(p) - \frac{1}{2} (J(k, k+p) + J(k', k'+p)) \right] M(k, k+p) M(k', k'+p), \quad (A.2a)$$

$$B_p(k, k') = \frac{1}{\Omega} \left[v(k - k' + p) - \frac{1}{2} (J(k', k+p) + J(k, k' - p)) \right] M(k', k+p) M(k, k' - p) + \frac{1}{\Omega} \left[v(p) - \frac{1}{2} (J(k, k+p) + J(k', k' - p)) \right] M(k, k+p) M(k', k' - p), \quad (A.2b)$$

where

$$L(k, k') = u_k u_{k'} - v_k v_{k'}, \quad (A.3)$$

$$M(k, k') = u_k v_{k'} + v_k u_{k'}.$$

It can immediately be seen that in Eq. (A.1) the second terms of (A.2a, b) cancel out each other, and the direct Coulomb interactions $v(p)$ does not enter the equation of continuity, and thus does not affect the gauge invariance.

Now, we calculate the quantity in the curled bracket in Eq. (A.1), and we obtain

$$(uv' + u'v)W_p(\mathbf{k}) + (uu' + vv') \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') (2u_{\mathbf{k}'}v_{\mathbf{k}} + u_{\mathbf{k}'+\mathbf{p}}v_{\mathbf{k}'+\mathbf{p}} - u_{\mathbf{k}'+\mathbf{p}}v_{\mathbf{k}'-\mathbf{p}}) - \frac{1}{2}(uv' - u'v) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') (v_{\mathbf{k}'+\mathbf{p}}^2 - v_{\mathbf{k}'+\mathbf{p}}^2), \quad (\text{A.4})$$

where we write $u_{\mathbf{k}} \equiv u$, $u_{\mathbf{k}+\mathbf{p}} \equiv u'$ etc. and

$$V(\mathbf{k}, \mathbf{k}') = \frac{1}{\Omega} \left(v(\mathbf{k}' - \mathbf{k}) - \frac{1}{2}(J(\mathbf{k}, \mathbf{k}') + J(\mathbf{k} + \mathbf{p}, \mathbf{k}' + \mathbf{p})) \right). \quad (\text{A.5})$$

If we expand Eq. (A.4) in power series of p , it is easily seen that the third term is of the order of or higher than p^3 . The constant terms of the first and second terms cancel out each other (the summation over $\mathbf{k}'$ in the second term is nothing but the energy gap). The term of the order of p^2 in these terms become

$$\frac{\epsilon_0}{2E_{\mathbf{k}}^2} (\epsilon_{\mathbf{k}+\mathbf{p}} - \epsilon_{\mathbf{k}})^2 = \frac{\epsilon_0}{2E_{\mathbf{k}}} \left(\frac{\hbar^2}{m} (\mathbf{k}, \mathbf{p}) \right)^2, \quad (\text{A.6})$$

if the B.C.S. approximation, $V(\mathbf{k}, \mathbf{k}') \sim \text{const.}$ is used.

On the other hand $\hbar/e \cdot \mathbf{p} \cdot \mathbf{j}_0(\mathbf{p})$ can be written as

$$\begin{aligned} \frac{\hbar}{e} \mathbf{p} \cdot \mathbf{j}_0(\mathbf{p}) &= \frac{\hbar^2}{m} \sum_{\mathbf{k}} \mathbf{p} \cdot \left(\mathbf{k} + \frac{1}{2}\mathbf{p} \right) (u'v - uv') (\beta_{\mathbf{p}^+}(\mathbf{k}) - \beta_{-\mathbf{p}}(\mathbf{k} + \mathbf{p})) \\ &= \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}+\mathbf{p}} - \epsilon_{\mathbf{k}}) (u'v - uv') (\beta_{\mathbf{p}^+}(\mathbf{k}) - \beta_{-\mathbf{p}}(\mathbf{k} + \mathbf{p})). \end{aligned} \quad (\text{A.7})$$

Because $u'v - uv' = \epsilon_0/2E_{\mathbf{k}} \cdot (\epsilon_{\mathbf{k}+\mathbf{p}} - \epsilon_{\mathbf{k}})$, (A.7) coincides with (A.1).

References

- 1) J. Bardeen, L. Cooper and J. Schrieffer: Phys. Rev. **108** (1957) 1175.
- 2) P. W. Anderson: Phys. Rev. **110** (1958) 827.
- 3) K. Yosida: Progr. Theor. Phys. **21** (1959) 731.
- 4) N. N. Bogoliubov: J. Exp. Theor. Phys. U.S.S.R. **34** (1958) 68.
- 5) G. Wentzel: Phys. Rev. **111** (1958) 1488.
- 6) F. J. Dyson: Phys. Rev. **102** (1956) 1217.
- 7) M. Gell-mann and K. A. Bruckner: Phys. Rev. **106** (1957) 364. K. Sawada: Phys. Rev. **106** (1957) 372.
- 8) G. Wentzel: Phys. Rev. **108** (1957) 1593.
- 9) T. Nishiyama: Progr. Theor. Phys. **21** (1959) 389.
- 10) H. Kanazawa and N. Matsudaira: Progr. Theor. Phys. (in press)

Breakdown of Argon at Low Pressure in a Longitudinal Magnetic Field

By Kenji MITANI and Hiroshi KUBO

Yoshida College, University of Kyoto

(Received July 29, 1959)

We measured the breakdown probability at a low pressure in argon over the range from 0 to 1,500 gauss of the magnetic field parallel to the electric field. With the overvoltage fixed at 16.5%, the number of times of breakdown was counted for the applied square pulses with an electronic counter. Thus we found that the breakdown probability increased with magnetic field intensity. We calculated the breakdown probability on the assumption that breakdown was caused by multi-avalanche, and the secondary mechanism was due to the drift of resonance radiation in the diffusion process as Kachikas and Fisher had suggested. A fairly good agreement between theory and experiment was attained and the drift velocity of resonance radiation was about 9.5×10^6 cm. sec⁻¹ in our calculation.

§ 1. Introduction

So far as we are aware, only a few remarkable results of experiments on the gas breakdown in a magnetic field have been reported¹⁾. We examined into the effect of the magnetic field parallel to the electric field in a uniform gap upon the low pressure gas breakdown caused by d.c. pulse. It might be expected that such a magnetic field has no effect on the breakdown, but it really has.

In our experiment, the effect of magnetic field upon the gas breakdown was observed by measuring the breakdown probability. The breakdown probability, i.e., the probability that the breakdown occurs in a given time interval, is considered to be a function of the formative time lag alone, when all the experimental conditions are kept unvaried excepting the magnetic field intensity²⁾. So we will first have a theoretical consideration on the effect of the longitudinal magnetic field upon the formative time lag. The time lag in the absence of magnetic field has been discussed by many authors^{2), 3)}; of their theories, most well-known is Fletcher's⁴⁾, in which the formative time lag of a single avalanche in the air of atmospheric pressure is discussed. We have so modified his method as to fit the multi-avalanche in a longitudinal magnetic field, thereby having succeeded in explaining the results of our experiment.

§ 2. Theory

Firstly we calculate the formative time lag

t_f for argon with small $p\delta$, the pressure times the gap distance, in a longitudinal magnetic field under a moderate overvoltage. It is not sufficient to rely only on α - and γ -mechanisms to examine into the present case of breakdown, because they are hardly influenced by the longitudinal magnetic field⁵⁾. So we are led to take into account the electron diffusion, which is conspicuously influenced by the longitudinal magnetic field. So far, many authors have discussed about the build-up mechanism of electric discharges^{6), 7)}. Of them, Bartholomeyczuk took into account the diffusion corresponding to the edge-effect, though the build-up of electric discharge takes place all over the gap⁸⁾. We apply, however, Fletcher's theory because of its special fitness for our case. Fletcher's theory is concerned with the atmospheric pressure, and hence it deals only with a single avalanche, but in our case the multi-avalanche must be considered because of small $p\delta$.

Another difficulty in our case is in understanding the secondary mechanism of electric breakdown in argon. It is known from many authors^{9), 10)} that the electron emission mechanism from the cathode in the breakdown of argon, which is called the γ -mechanism, generally arises from the bombardment of the cathode by ions, metastable atoms, and photons. In 1951, J. P. Molnar discussed in detail of these mechanism¹⁰⁾. Thereafter in 1953, G. A. Kachikas and L. H. Fisher concluded¹¹⁾, from the study of formative time lags of uni-

form field breakdown in argon, that diffusion of resonance radiation played an important rôle in the breakdown of argon and its average transit time was about ten times that of the electron. Following their suggestion, we considered only the effect of photons in the calculation of the breakdown probability with magnetic field.

Then the breakdown is considered to take place in the following process: primary electron leaving the cathode produces an avalanche while proceeding to the anode with the velocity v , but for low $p\delta$ a single avalanche is unable to create a space charge field high enough to cause breakdown. Therefore the photons produced just before the anode drift back to the cathode by diffusion mechanism of resonance radiation with the velocity V , of which the magnitude will be determined from our theory and experimental data. At the anode they liberate the electrons initiating the secondary avalanche. Thereafter the same process is repeated till the space charge field high enough to cause breakdown is attained. In this way one ionization cycle t_i , after the notation of Druyvestyn and Penning¹²⁾, is given by

$$t_i = \frac{\delta}{v} + \frac{\delta}{V} = \tau_e + \tau_p, \quad (1)$$

where τ_e and τ_p are respectively the transit times of electrons and photons across the gap spacing δ .

Then we consider the multiplication factor M which is the number of electrons liberated at the cathode due to one electron which has started from the cathode before one ionization cycle t_i . This factor for argon is very complicated. However, as mentioned above, here we consider only the effect of photons. For the multiplication factor by photons we adopt the following form given by Hasebe and Yamamoto¹³⁾:

$$M = \gamma_p f_1 f_2 \{ \exp(\alpha \delta) - 1 \}, \quad (2)$$

where γ_p is the number of electrons released at the cathode per photon and α is the number of electron-ion pairs generated per electron per cm of path in a direction perpendicular to the electrode surfaces and is called Townsend's first coefficient. The factor f_1 is the number of photons per ion formed in the gas and is explicitly given by the following expression for argon with reference to Molner's

experimental data^{10), 13)}:

$$f_1 = 0.1875 \exp(144.5 p/E), \quad (3)$$

where E is the electric field intensity in volts per cm, and p is the pressure in mm Hg. The factor f_2 is the probability that an avalanche goes on in the track of the foregoing avalanche; and, in the absence of the magnetic field, it is given by $(r/\delta)^2$, where r is the avalanche radius just before the anode¹³⁾. This is obtained under the assumption that photons travel uniformly in all directions from the tip of the avalanche just before the anode, and the avalanche is in the form of sphere. In our case, however, we must consider the effect of longitudinal magnetic field upon the form of avalanche and the process of diffusion of resonance radiation. In such a field, which will be discussed later, the avalanche is not spherical but in the form of prolate spheroid with the major axis parallel to the magnetic field. From this point of view, f_2 is supposed to be smaller than in the absence of magnetic field. We know, however, little about the mechanism of resonance radiation and still less we have the knowledge of the effect of longitudinal magnetic field upon the process of diffusion of resonance radiation. So we approximately assume that the factor f_2 is independent of longitudinal magnetic field and is expressed by the same form as that in the absence of magnetic field. Now, r is given by $(6D\tau_e)$ where D and τ_e are respectively the coefficient of diffusion and the transit time of electrons⁹⁾, so the factor f_2 becomes

$$f_2 = (r/\delta)^2 = 6D\tau_e/\delta^2 = 6D/v\delta = 3a/2\delta, \quad (4)$$

where v is the drift velocity of electrons and $a = 4D/v$ is the characteristic length which is almost independent of the applied electric field intensity E ⁹⁾.

In terms of the multiplication factor M given above, the number N of electrons, which one electron leaving the cathode at $t=0$ produces at the time qt_i , is expressed after Druyvestyn and Penning¹²⁾ by

$$N = (M^{qt_i+1} - 1)/(M - 1), \quad (5)$$

which is transformed for $M^{qt_i+1} \gg 1$ into

$$q = \{ \ln N(M-1) / \ln M \} - 1. \quad (6)$$

Then we calculate the critical avalanche size N_0 . We take cylindrical coordinate with the origin at the cathode and z -axis in the direction to the anode. The diffusion coefficient D_n

in the direction perpendicular to the magnetic field is calculated to be^{(14), (15)}

$$D_n = D / \left(1 + \frac{\omega_b^2}{\nu_o^2} \right) \equiv D / (1 + k^2), \quad (7)$$

where D is the usual diffusion coefficient in the z -direction, $\omega_b = eH/cm$ the cyclotron frequency and ν_o the electron collision frequency and ω_b/ν_o is denoted by k . Then the rate of growth of electrons and that of positive ions are obtained from the following equations:

$$\left. \begin{aligned} \frac{\partial n_-}{\partial t} &= \alpha v n_- + \frac{D}{1+k^2} \left(\frac{1}{r} \frac{\partial n_-}{\partial r} + \frac{\partial^2 n_-}{\partial r^2} \right) \\ &\quad + D \frac{\partial^2 n_-}{\partial z^2} - v \frac{\partial n_-}{\partial z}, \\ \frac{\partial n_+}{\partial t} &= \alpha v n_+. \end{aligned} \right\} \quad (8)$$

From these we obtain the following exact solutions,

$$\left. \begin{aligned} n_- &= (4\pi Dt)^{-3/2} \exp \left[-\frac{(1+k^2)r^2 + (z-vt)^2}{4Dt} + \alpha vt \right], \\ n_+ &= \alpha v \int_0^t n_-(t') dt'. \end{aligned} \right\} \quad (9)$$

Since the equation (9) for $k=0$, that is in the absence of the magnetic field, was discussed in detail in Fletcher's paper⁽⁴⁾, we only apply its results to our case. From Eq. (9) the electron avalanche is supposed to be in the form of prolate spheroid with the major axis along the magnetic field and the center at $z_0 = vt$, leaving the positive ions in a cone-shaped volume behind it as shown in Fig. 1. For convenience' sake, we consider the effective avalanche radius r_D . From the electron distribution obtained above, it can be calculated

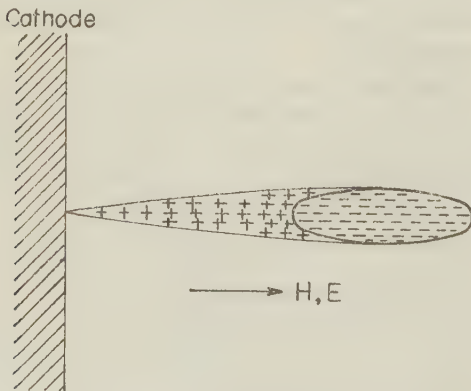


Fig. 1. Electron avalanche in the longitudinal magnetic field.

as follows:

$$\begin{aligned} r_D &= \frac{\int_{-\infty}^{+\infty} \int_0^{\infty} (r^2 + z'^2) n - 2\pi r dr dz'}{\int_{-\infty}^{+\infty} \int_0^{\infty} n - 2\pi r dr dz'} \\ &= \{ (3+k^2)/3(1+k^2)^2 \}^{1/2} (6Dt)^{1/2} \equiv A^{1/2} (6Dt)^{1/2} \end{aligned} \quad (10)$$

where z' denotes the moving coordinate with the center at $z_0 = vt$, and t is the time measured from the instance at which the primary electron leaves the cathode; and it is noticed that the time t should be put into $q\tau_e$ where τ_e is the transit time of electrons across the gap and q is given by (6), because the avalanche is produced while the electrons go forward to the anode but not while the resonance radiations drift back to the anode. $(6Dt)^{1/2}$ is the avalanche radius in the absence of the

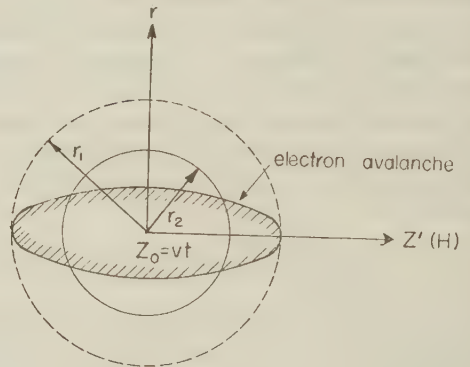


Fig. 2. Electron avalanche radius with and without magnetic field. r_1 : without magnetic field; r_2 : with magnetic field.

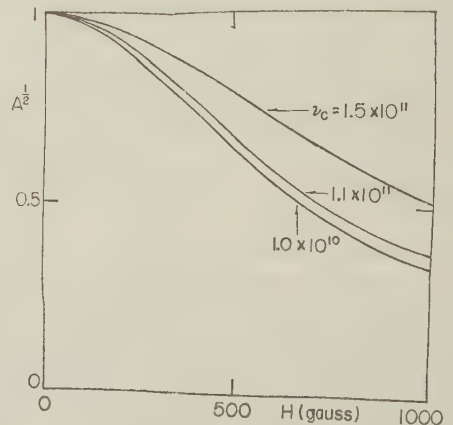


Fig. 3. Ratio of the effective avalanche radius with magnetic field to the normal one without it, $A^{1/2}$, as a function of the magnetic field intensity H .

magnetic field. We find from Eq. (10) that the avalanche radius in the longitudinal magnetic field decreases with its intensity increasing, as shown in Fig. 2 and Fig. 3; in other words the electron density increases with the magnetic field intensity.

It is expected that the space charge field becomes active after some increase of the densities of electrons and ions by ionization, and the distributions of them become different from the expressions (9). In that state the drift velocity of electrons mainly depends on the diffusion, and the diffusion velocities v_z and v_r along z - and r -axes are respectively represented by the following expressions,

$$\left. \begin{aligned} v_z &= -\frac{D}{n_-} \frac{\partial n_-}{\partial z'} = \frac{z'}{2t}, \\ v_r &= -\frac{D}{1+k^2 n_-} \frac{1}{\partial r} \frac{\partial n_-}{\partial r} = \frac{r}{2t}, \end{aligned} \right\} \quad (11)$$

where z' and t have the same meaning as those above mentioned. On averaging out, by the same way as Eq. (10), the resultant velocity obtained from the above results, the drift velocity v_t of electrons at the time t_t , when the space charge first becomes important, is calculated as

$$v_t = r_{Dt}/2t_t, \quad (12)$$

where the suffix t , following the Fletcher's notation, denotes the values at the time t_t . From (1) and (6), this time is expressed by

$$\left. \begin{aligned} t_t &= q_e \tau_e \\ &= \frac{\delta}{v} \{ \ln N_t(M-1) / \ln M - 1 \}, \end{aligned} \right\} \quad (13)$$

where N_t is the number of electrons at the time t_t . If we assume, after Fletcher^(4),9), a general relation $v \sim (E)^{1/2}$ between the electric field E and the drift velocity v of electrons due to it, the relation between the space charge field intensity E_t corresponding to N_t and the applied field E can be expressed from (12) and (13):

$$E_t = A \frac{3}{8} \frac{a}{\delta} \frac{\ln M}{\ln N_t(M-1) - \ln M} E. \quad (14)$$

Another relation between E_t and N_t can be calculated as follows. Following Fletcher's discussion of (9) when $H=0$, we can assume that the positive ions are distributed in a sphere of the same radius r_{Dt} as the electrons, and the distance between the centers of ions and electron spheres is $1/\alpha$. The maximum Coulomb field intensity for $r_{Dt} > 1/\alpha$ can be

approximately calculated from the above distributions by aid of (6) as follows:

$$E_t = \frac{e}{4\pi\epsilon_0} \frac{N_t}{\alpha} \left\{ \frac{2 \ln M}{3Aa\delta[\ln N_t(M-1) - \ln M]} \right\}^{3/2}, \quad (15)$$

where e is the charge of electron and ϵ_0 the dielectric constant of free space (in rational m.k.s. units). By eliminating E_t from (14) and (15), N_t becomes:

$$N_t = \frac{9}{16} \frac{1}{300} \frac{1}{e} EA^2 a^2 \alpha \left[\frac{3}{2} Aa\delta \frac{\ln N_t(M-1)}{\ln M} - 1 \right]^{1/2}. \quad (16)$$

Furthermore, by using the relations (6), (13), (14) and the relation $v \sim (E)^{1/2}$ mentioned previously, we obtain the space charge field E_s at the time t_s larger than t_t (for the time t_s Fletcher assumes that the field is proportional to the number N of electrons and inversely proportional to the square of the avalanche size r_{Ds} , where the suffix s denotes the value at the time t_s):

$$E_s = \frac{3}{16} A \frac{a}{\delta} E \left(\frac{N}{N_t} \right)^{1/2} \ln M \left/ \left[1 - \frac{\tan^{-1} N^{1/2}(M-1)^{1/2}}{N^{1/2}(M-1)^{1/2}} \right] \right. \quad (17)$$

For a large value of N , the second term of the denominator in the above equation can be approximated to zero. Thus (17) can be put into the following equation:

$$E_s = \frac{3}{16} A \frac{a}{\delta} E \left(\frac{N}{N_t} \right)^{1/2} \ln M. \quad (18)$$

The critical avalanche size N_0 is determined by setting $E=E_s$ in the above equation, that is,

$$N_0 = \frac{1}{A^2} \frac{256}{9} \frac{\delta^2}{a^2 (\ln M)^2} N_t. \quad (19)$$

By putting N_t from (16) into (19), we can calculate the value of the critical avalanche size N_0 corresponding to the applied electric field E and magnetic field H . Further by introducing this N_0 into (6), we can obtain q_0 corresponding to N_0 . Thus the formative time lag t_f can be determined from the following expression:

$$t_f = q_0 t_i, \quad (20)$$

where t_i is the ionization cycle given by (1).

Now, according to Wilson and Newman^(2),16), for the given statistical time lag T_s and the formative time lag t_f , the probability P that

the breakdown would occur by the time t after a certain overvoltage has been applied, is given by the following expression,

$$P = 1 - \exp\left(1 - \frac{t - t_f}{T_s}\right);$$

or, by introducing the relation (20) into this equation, we obtain

$$P = 1 - \exp\left(1 - \frac{t - q_0 t_i}{T_s}\right). \quad (21)$$

In our experiment, which will be described in the next section, the probability P was measured by counting the number of times of breakdown really occurring for a train of square pulses with a definite pulse width. The pulse width may be considered to correspond to the time t in (21). If all the experimental conditions excepting the magnetic field intensity H are kept constant, we can consider t_i and T_s in (21) to be constant, so the probability P might be considered to change only through q_0 corresponding to the magnetic field intensity.

§ 3. Experimental Procedure and Results

The electrodes used in our experiment are of copper 2.1 cm in diameter. Their faces were polished with finest emery paper and then cleaned with benzene petroleum. The sparking gap length δ is about 2.5 mm. The discharge tube was evacuated to about 10^{-6} mm Hg and then filled with argon labelled "pure" but its purity was not affirmed in our laboratory. The pressure of argon was 20.5 mm Hg and was kept constant throughout the experiment. Furthermore, the tube was

set in a solenoidal coil, whose maximum magnetic field intensity was 1,500 gauss.

First, we measured the threshold breakdown voltage V_s with and without the longitudinal magnetic field, and we found that the values were the same 285 volts in both cases. On the basis of the breakdown criterion $\gamma_p e^{\alpha \delta} = 1^{(6)}$, this fact shows that the Townsend's First Coefficient α as well as Second Coefficient γ_p is independent of the magnetic field intensity.

The block diagram of the apparatus used in the experiment is shown in Fig. 4. In order to cause breakdown in the gap, we applied square pulses, whose rise time was of the order 10^{-2} μ sec, pulse height 332 volts (that is, the overvoltage $\Delta = 16.5\%$), repetition frequency 1.13 sec^{-1} and pulse width 20 μ sec. These values were kept constant throughout the experiment. The electrodes were irradiated with γ -ray from Ra-B.

To measure the breakdown probability P , we counted the number of the breakdowns n occurring during a definite time interval; on the other hand the total number of the square pulses n_T applied during that time interval

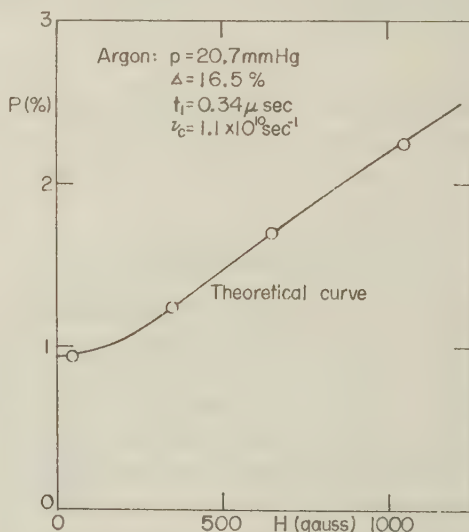


Fig. 5. Breakdown probability as a function of longitudinal magnetic field intensity H (gauss). $\circ$: experimental values.

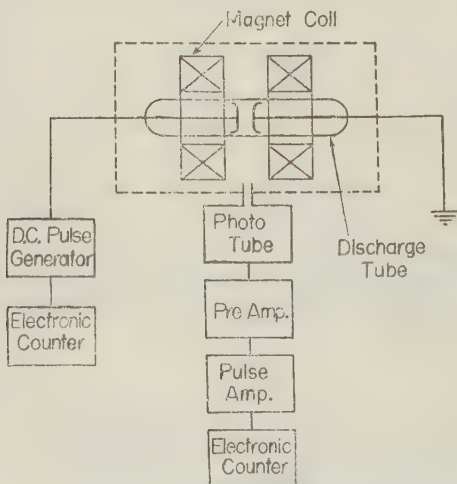


Fig. 4. Block diagram of experimental apparatus.

was calculated from the repetition frequency. Then the breakdown probability P is expressed by the expression $P = n/n_T$. Experimental results obtained by us are plotted by open circles in Fig. 5. From this figure we find that the breakdown probability increases with the magnetic field intensity H .

4. Discussion

The constants used for our calculation are given in the following.

(1) γ_p : From the measured threshold voltage $V_s=285$ volts, E_s/p is 55 volts cm^{-1} . mmHg^{-1} . The value of α for this E_s/p is 16.35 cm^{-1} from the data by Druyvestyn and Penning¹⁷⁾. From this value and the breakdown criterion $\gamma_p e^{\alpha d}=1$, γ_p is calculated to be 1.68×10^{-2} . This is a reasonable value in comparison with Kruithoff's¹⁸⁾. And, generally speaking, γ_p does not vary very much over a wide range of overvoltage¹⁸⁾, thus we used $\gamma_p=1.68 \times 10^{-2}$ in our calculation for overvoltage $\Delta=16.5\%$.

(2) f_1 : From the Molner's relation (3), $f_1=1.785$ is obtained in our case for $E/p=64$ volts cm^{-1} . mmHg^{-1} .

(3) a and f_2 : From the relation $D/v=0.25/p$ for argon¹⁹⁾, $a (=4D/v)$ is $5 \times 10^{-2} \text{ cm}$. Accordingly, by using this value, $f_2=0.3$ is obtained from (6).

(4) M : By putting the above values of γ_p , f_1 and f_2 into Eq. (4), the multiplication factor M for the breakdown voltage $V=332$ volts (accordingly the overvoltage $\Delta=16.5\%$) becomes 1.58.

There are still two more unknown factors necessary to calculate the probability P as a function of H ; one is the collision frequency of electrons ν_e in (7), and the other the time t_i in (1). To obtain a good agreement between theory and experiment, we had to adopt $\nu_e=1.1 \times 10^{10} \text{ sec}^{-1}$ and $t_i=0.34 \mu\text{sec}$. A solid curve in Fig. 5 shows the result calculated by using the above values and the theory mentioned in the preceding section. Fig. 6 shows the formative time lag t_f and the critical avalanche size N_c corresponding to the above result. As shown in this figure, the formative time lag for $H=0$ is about $19 \mu\text{sec}$. On the other hand, a corresponding value obtained by extrapolating experimental results by Kachikas and Fisher¹¹⁾ is about $16 \mu\text{sec}$. Agreement between them might be said to be fairly good.

Furthermore, we can evaluate the drift velocity V of resonance radiation of argon by using the value $t_i=0.34 \mu\text{sec}$. The calculation gives about $9.5 \times 10^5 \text{ cm} \cdot \text{sec}^{-1}$ to it. This value is a little smaller than the drift velocity of electrons $v=3.66 \times 10^6 \text{ cm} \cdot \text{sec}^{-1}$ ²⁰⁾ but larger than that of ions (A^+) $v_i=5 \times 10^4 \text{ cm} \cdot \text{sec}^{-1}$ for $E/p=64$ volts cm^{-1} . mmHg^{-1} ²¹⁾. This result accords with the qualitative statement by

Kachikas and Fisher¹¹⁾ from their experiments that the drift velocity of resonance radiation is smaller than that of electron but larger than that of ion.

Thus we have theoretically explained the breakdown probability as a function of the longitudinal magnetic field and succeeded in inferring an approximate value of the drift velocity of resonance radiation by diffusion process.

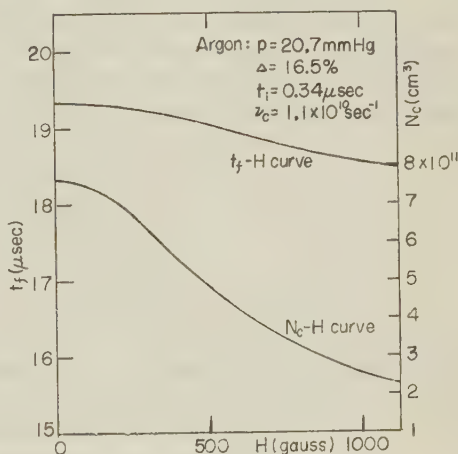


Fig. 6. Formative time lag t_f and critical avalanche size N_c versus the magnetic field intensity H .

In conclusion, the authors gratefully acknowledge their indebtedness to Professor K. Honda of Tokyo University, Professor Y. Miyoshi of Nagoya Technical College and their groups for their encouragement and helpful discussions. The authors thanks are also due to Professor I. Takahashi of Kyoto University for his kind suggestion and discussion.

References

- 1) G. Francis: *Handbuch der Physik*, vol. **22** (Springer-Verlag, Berlin, 1956) 164.
- 2) L. B. Loeb: *Handbuch der Physik*, vol. **22** (Springer-Verlag, Berlin, 1956) 469-480.
- 3) J. M. Meek and J. D. Craggs: *Electrical Breakdown of Gases* (Oxford Univ. Press, London, 1953)
- 4) R. C. Fletcher: *Phys. Rev.* **76** (1949) 1501.
- 5) L. B. Loeb: *Handbuch der Physik*, vol. **21** (Springer-Verlag, Berlin, 1956) 570.
- 6) L. B. Loeb: loc. cit. vol. **22**, 445-469.
- 7) Y. Miyoshi: Reports of Nagoya Technical College, (in Japanese) **4** (1952) 1; **6** (1954) 1.
- 8) W. Bartholomeyczuk: *Z. Phys.* **116** (1940) 235.

- 9) L. B. Soeb: *Basic Processes of Gaseous Electronics* (Univ. of California Press, Barkley and Los Angeles, 1955)
- 10) J. P. Molner: *Phys. Rev.* **83** (1951) 933.
- 11) G. A. Kachikas and L. H. Fisher: *Phys. Rev.* **91** (1953) 775.
- 12) M. J. Druyvestyn and F. M. Penning: *Rev. Mod. Phys.* **12** (1940) 87.
- 13) K. Hasebe and K. Yamamoto: *J. I. E. E. Japan* **78** (1958) 751.
- 14) L. Tonks: *Phys. Rev.* **51** (1937) 744.
- 15) J. S. Townsend: *Phil. Mag.* **25** (1938) 259.
- 16) R. R. Wilson: *Phys. Rev.* **50** (1936) 1082.
M. Newman: *Phys. Rev.* **52** (1937) 657. R. A. Wijsman: *Phys. Rev.* **75** (1949) 833.
- 17) M. J. Druyvestyn and F. M. Penning: *loc. cit.*
- 18) A. A. Kruithoff: *Physica* **7** (1940) 519. L. B. Loeb: reference (19), p. 846.
- 19) M. Hayashi: Private communication. A. A. Kruithoff and F. M. Penning: *Physica* **3** (1936) 515; **4** (1937) 430; **5** (1938) 203. A. D. MacDonald and J. H. Matthews: *Phys. Rev.* **98** (1955) 1070.
- 20) R. A. Nielson: *Phys. Rev.* **50** (1936) 950. L. Colli. and U. Facchini: *Rev. Sci. Instr.* **23** (1952) 39. J. M. Kirshner and D. S. Toffolo: *J. Appl. Phys.* **23** (1952) 594.
- 21) L. B. Loeb: *Phys. Rev.* **102** (1957) 1219. M. A. Biondi and L. M. Charin: *Phys. Rev.* **94** (1954) 910. J. A. Hornbeck: *Phys. Rev.* **84** (1951) 615.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4 APRIL, 1960,

Ion-Electron Relaxation of Plasmas in a Magnetic Field, II.

By Taro KIHARA, Yukio MIDZUNO, Kyoko SAKUMA
and Toshio SHIZUME

*Department of Physics, Faculty of Science,
University of Tokyo*

(Received December 5, 1959)

Relaxation between ion and electron temperatures, T_1 and T_2 , of dilute fully ionized gases in a magnetic field has been treated by force-correlation method. The rate R of the relaxation, defined by

$$d(T_2 - T_1)/dt = -(T_2 - T_1)R,$$

increases with increasing magnetic field from

$$R = R^0 \ln(t_p/t_s) \quad \text{for } \omega_2 t_p \lesssim 1$$

$$\text{to } R = R^0 [\ln(t_p/t_s) + \frac{1}{2}(\ln \omega_2 t_p)^2] \quad \text{for } \omega_2 t_p \gg 1,$$

in which

$$R^0 = (n_1 + n_2)(8m_2/3m_1)(2\pi k T_2/m_2)^{1/2}(Ze^2/kT_2)^2.$$

Here m_1 , Ze and n_1 are the mass, charge and number density of the ion respectively; m_2 , $-e$, and n_2 are those of the electron; t_p is the period of plasma oscillation and t_s is the mean time of passage through a sphere of strong interaction, $t_s \sim (m_2/kT_2)^{1/2}Ze^2/kT_2$; ω_2 is the electron gyration frequency.

§1. Introduction

The ion-electron relaxation of a fully ionized gas in a magnetic field has been treated in Part I¹⁾ by an elementary method under the restriction that field is extremely strong. In part II the phenomenon will be treated more systematically without this restriction. The result obtained in Part I is included in the

present part as a special case. Since the mass ratio of an ion to an electron is far from unity, energy transfer between ion and electron is much smaller than that between electrons. Hence the ion temperature T_1 and the electron temperature T_2 are often different even when the velocity distribution are both uniform and Maxwellian. The rate R

of this relaxation is defined by

$$\frac{d}{dt}(T_2 - T_1) = -(T_2 - T_1)R \quad (1.1)$$

with time t .

The aim of this paper is to discuss the rate of relaxation in a fully ionized gas in a magnetic field. Both the gas and the magnetic field are assumed to be uniform in space. The gas is supposed to comprise one type of positive ion and electrons. The particle mass, particle charge and number density of the ion will be denoted by m_1 , Ze and n_1 respectively; those of electrons by m_2 , $-e$ and n_2 ($Zn_1 = n_2$, $Z^2 \ll m_1/m_2$). We consider the case where the mean ion velocity is much smaller than the mean electron velocity:

$$(T_1/m_1)^{1/2} \ll (T_2/m_2)^{1/2}. \quad (1.2)$$

The long-range many-body interaction characteristic of the coulomb potential r^{-1} can be eliminated by use of a shielded interparticle potential, say $r^{-1} \exp(-\kappa_{12}r)$. Although the shielding constant κ_{12} effective to the ion-electron relaxation can not be determined exactly, it is of the order of l_D^{-1} , l_D being the Debye's characteristic length. At high temperatures or low densities, i.e. for weak interactions, the rate of relaxation does not sensitively depend on the constant κ_{12} . We confine ourselves to this case.

§ 2. Formulation in Terms of the Force Correlation

The particle velocities of the ion and the electron will be denoted by $\mathbf{c}_1$ and $\mathbf{c}_2$, respectively, with $|\mathbf{c}_1| \equiv c_1$ and $|\mathbf{c}_2| \equiv c_2$. Since the average value of $m_1 c_1^2/3$ is kT_1 , the time rate of change of kT_1 is given by the average value of the time rate of change of $m_1 c_1^2/3$:

$$\frac{d}{dt}kT_1 = \frac{1}{3}m_1 \frac{1}{dt} \langle |\mathbf{c}_1 + \Delta \mathbf{c}_1|^2 - c_1^2 \rangle_{\text{Av}},$$

k being the Boltzmann constant, or

$$\frac{d}{dt}kT_1 = \frac{1}{3}m_1 \frac{1}{dt} \langle (2\mathbf{c}_1 + \Delta \mathbf{c}_1) \cdot \Delta \mathbf{c}_1 \rangle_{\text{Av}}. \quad (2.1)$$

Here $\Delta \mathbf{c}_1$ indicates the increment in ion velocity due to the interaction with surrounding electrons in the time interval dt ; dt must be much larger than the time characteristic of fluctuation of the interaction, yet much smaller than the relaxation time R^{-1} . $\langle \rangle_{\text{Av}}$ means the average with respect to the ion velocity and the interaction with surrounding electrons.

When the ion temperature T_1 is much smaller

than the electron temperature T_2 , the average value of $\mathbf{c}_1 \cdot \Delta \mathbf{c}_1$ can be neglected in comparison with the average value of $|\Delta \mathbf{c}_1|^2$; hence

$$\frac{d}{dt}kT_1 = \frac{1}{3}m_1 \frac{1}{dt} \langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}} \text{ for } T_1 \ll T_2. \quad (2.2)$$

The relation (2.2) can be generalized to

$$\frac{d}{dt}kT_1 = \frac{1}{3}m_1 \frac{1}{dt} \langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}} \frac{T_2 - T_1}{T_2} \quad (2.3)$$

which holds for T_1 satisfying (1.2). A proof, which was given in Part I, is the following. Since $m_1 \gg m_2$ the quantity $|\Delta \mathbf{c}_1|^2$ averaged with respect to the interaction with surrounding electrons is independent of $\mathbf{c}_1$; but $\Delta \mathbf{c}_1$ so averaged depends linearly upon $\mathbf{c}_1$. Hence, for constant T_2 , $\langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}}$ is independent of T_1 , and $\langle \mathbf{c}_1 \cdot \Delta \mathbf{c}_1 \rangle_{\text{Av}}$ is proportional to T_1 . Taking account of the fact that $\langle (2\mathbf{c}_1 + \Delta \mathbf{c}_1) \cdot \Delta \mathbf{c}_1 \rangle_{\text{Av}}$ vanishes for $T_1 = T_2$, we obtain

$$2\langle \mathbf{c}_1 \cdot \Delta \mathbf{c}_1 \rangle = -\langle T_1/T_2 \rangle \langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}},$$

by virtue of which (2.3) follows from (2.1). (Here we have neglected, under our assumption, the dependence of the shielding constant on the ion temperature.)

By use of the relationship

$$\frac{d}{dt}(n_1 T_1 + n_2 T_2) = 0,$$

the rate of relaxation R defined by (1.1) is calculated to

$$R = \frac{1}{3}(n_1 + n_2) \frac{m_1}{k T_2 n_2} \frac{1}{dt} \langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}}. \quad (2.4)$$

The increment in ion velocity during dt is given by

$$\Delta \mathbf{c}_1 = \frac{1}{m_1} \int_0^{dt} \tilde{\mathbf{F}}(\tau) d\tau,$$

where $\tilde{\mathbf{F}}(\tau)$ is the force acting on the ion at time τ . Hence

$$\begin{aligned} |\Delta \mathbf{c}_1|^2 &= \frac{1}{m_1^2} \int_0^{dt} \int_0^{dt} \tilde{\mathbf{F}}(\tau) \cdot \tilde{\mathbf{F}}(\tau') d\tau d\tau' \\ &= \frac{1}{m_1^2} \int_0^{dt} \int_{-\tau}^{dt-\tau} \tilde{\mathbf{F}}(\tau) \cdot \tilde{\mathbf{F}}(\tau+t) dt d\tau. \end{aligned}$$

Since dt is much larger than the continuance of the force correlation, we have

$$\frac{1}{dt} \langle |\Delta \mathbf{c}_1|^2 \rangle_{\text{Av}} = \frac{1}{m_1^2} \int_{-\infty}^{\infty} \langle \tilde{\mathbf{F}}(0) \cdot \tilde{\mathbf{F}}(t) \rangle_{\text{Av}} dt. \quad (2.5)$$

The force acting on an ion is the sum of contributions from all the surrounding electrons

$$\tilde{\mathbf{F}}(t) = \sum_i \mathbf{F}^i(t),$$

$\mathbf{F}^i$ indicating the force due to i th electron. Since the long-range many-body interaction has been eliminated by use of a shielded interparticle potential, the force due to an electron is independent of force due to other electrons, namely

$$\langle \tilde{\mathbf{F}}(0) \cdot \tilde{\mathbf{F}}(t) \rangle_{AV} = \langle \sum_i \mathbf{F}_i(0) \cdot \mathbf{F}^i(t) \rangle_{AV},$$

the cross terms vanishing. We have therefore

$$\int_{-\infty}^{\infty} \langle \tilde{\mathbf{F}}(0) \cdot \tilde{\mathbf{F}}(t) \rangle_{AV} dt = \iiint \mathbf{F}(0) \cdot \mathbf{F}(t) f_2 d\mathbf{c}_2 d\mathbf{r} dt, \quad (2.6)$$

in which $\mathbf{F}(t)$ is force due to an electron at time t and f_2 is the velocity distribution function for electrons,

$$f_2 = n_2 \left(\frac{m_2}{2\pi k T_2} \right)^{3/2} \exp \left(-\frac{m_2 c_2^2}{2k T_2} \right). \quad (2.7)$$

Here $\mathbf{r}$ and $\mathbf{c}_2$ are the position and the velocity at time 0 which the electron should have in the absence of the interaction.

Thus we obtain, from (2.4), (2.5) and (2.6)

$$R = \frac{1}{3} \frac{n_1 + n_2}{k T_2 n_2 m_1} \iiint \mathbf{F}(0) \cdot \mathbf{F}(t) f_2 d\mathbf{c}_2 d\mathbf{r} dt, \quad (2.8)$$

which is our basic relation.

§ 3. Correspondence with the Kinetic Theory

The aim of this section is to transform, in the absence of magnetic field, into a form which is familiar in the kinetic theory of gases.

Taking the coordinate-origin at the position of the ion and taking z -axis in the direction of the initial velocity $\mathbf{c}_2$ of an encountering electron, let us introduce the cylindrical coordinate (b, ϕ, z) for which

$$d\mathbf{r} = b db d\phi dz \quad (0 \leq b, 0 \leq \phi < 2\pi, -\infty < z < \infty)$$

b being the impact parameter. Thus

$$R = \frac{2\pi n_1 + n_2}{3 k T_2 n_2 m_1} \iiint \mathbf{F}(0) \cdot \mathbf{F}(t) dt dz b db f_2 d\mathbf{c}_2. \quad (3.1)$$

Now, since $-\mathbf{F}(t)$ is the force acting on the encountering electron, we have

$$\left| \int_{-\infty}^{\infty} \mathbf{F}(t) dt \right| = 2m_2 c_2 \sin \frac{\theta}{2},$$

θ being the angle of diffraction of the electron orbit. Further

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathbf{F}(0) \cdot \mathbf{F}(t) dt dz &= c_2 \left| \int_{-\infty}^{\infty} \mathbf{F}(t) dt \right|^2 \\ &= 2m_2^2 c_2^3 (1 - \cos \theta). \end{aligned}$$

Hence

$$R = \frac{(4\pi)^2}{3} \frac{n_1 + n_2}{k T_2 n_2} \frac{m_2^2}{m_1} \int_0^\infty \int_0^\infty (1 - \cos \theta) c_2^3 f_2 b db d\mathbf{c}_2. \quad (3.2)$$

The expression (3.2) can also be derived directly from (2.4). The increment in ion velocity $\Delta \mathbf{c}_1$ is sum of contributions from all the surrounding electrons. When these contributions are not correlated with each other, we have

$$\frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1|^2 \rangle_{AV} = 2\pi \int \int |\delta \mathbf{c}_1|^2 c_2 f_2 b db d\mathbf{c}_2,$$

in which $\delta \mathbf{c}_1$ is the increment due to one electron. The velocity increment of the electron is $-(m_1/m_2)\delta \mathbf{c}_1$, whose absolute value is equal to $2c \sin(\theta/2)$; thus we obtain (3.2).

It is to be noted that the kinetic formula (3.2) follows from the Boltzmann equation²⁾ without using the basic relation (2.4).

For the effective interparticle potential

$$Ze^2 r^{-1} \exp(-\kappa_{12} r) \quad (3.3)$$

between an ion and an electron, the integral in (3.2) has been calculated by Kihara²⁾ and Liboff³⁾. By use of it we have

$$R = R^0 \ln(3k T_2 / 4Ze^2 \kappa_{12}) \quad (3.4)$$

with

$$R^0 = \frac{8}{3} (n_1 + n_2) \frac{m_2}{m_1} \left(\frac{2\pi k T_2}{m_2} \right)^{1/2} \left(\frac{Ze^2}{k T_2} \right)^2. \quad (3.5)$$

Here an irrational number close to 3/4 has been replaced by 3/4 in the argument of the logarithm.

The expression (3.4) is exact as a weak-interaction asymptote for $k T_2 / Ze^2 \kappa_{12} \gg 1$ so far as the effective potential (3.3) is assumed. When the plasma is so hot and dilute that $\ln(k T_2 / Ze^2 \kappa_{12})$ is much larger than unity, the formula (3.4) is approximated by

$$R = R^0 \ln(k T_2 l_D / Ze^2), \quad (3.6)$$

in which l_D is the Debye length.

In order to obtain the limiting expression (3.6), it is sufficient to make integration of (3.1) or (3.2) over the domain of "weak interaction without correlation" $Ze^2/k T_2 \lesssim b \lesssim l_D$ only.

The integral $\iint \mathbf{F}(0) \cdot \mathbf{F}(t) dt dz$ in this domain becomes

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{b}{(b^2 + z^2)^{3/2}} \frac{b}{[b^2 + (z + c_2 t)^2]^{3/2}} dt dz = \frac{4}{b^2 c_2}$$

and, after integration with respect to $\mathbf{c}_2$, (3.1) is reduced to

$$R - R^0 \int_{Ze^2/kT_2}^{l_D} \frac{db}{b},$$

which is equal to (3.6).

In the present article this kind of approximation will be used throughout.

§ 4. Relaxation in a Magnetic Field

Returning to (2.8) let us discuss the rate of relaxation in a magnetic field. We assume that the mean electron gyration radius r_g is larger (but not necessarily much larger) than the limit of weak interaction Ze^2/kT_2 . For our purpose it is sufficient to make integration of (2.8) over the domain of "weak interaction without correlation". This domain is characterized, this time, by

$$t_s \leq |t| \leq t_p,$$

where t_p is the period of plasma oscillation, and t_s is the mean time of passage through a sphere of strong interaction, namely

$$t_p \sim \left(\frac{m_2}{kT_2}\right)^{\frac{1}{2}} l_D, \quad t_s \sim \left(\frac{m_2}{kT_2}\right)^{\frac{1}{2}} \frac{Ze^2}{kT_2}. \quad (4.1)$$

Thus, when coordinate origin is taken at the position of the ion, $F(0)$ is simply equal to $Ze^2 r/|r|^3$. As for $F(t)$, it is given by

$$F(t) = Ze^2 \frac{r + s(t, c_2)}{|r + s(t, c_2)|^3},$$

where $s(t, c_2)$ is the increment in the position vector during the time t when the electron velocity is c_2 at $t=0$:

$$s(0, c_2) \equiv 0, \quad \left[\frac{ds(t, c_2)}{dt} \right]_{t=0} \equiv c_2.$$

First, the relation

$$\int \frac{r}{|r|^3} \cdot \frac{r+s}{|r+s|^3} dr = \frac{4\pi}{|s|} \quad (4.2)$$

will be proved. The volume integral in the left-hand side of (4.2),

$$-\int \frac{r}{|r|^3} \cdot \nabla \frac{1}{|r+s|} dr$$

can be transformed into an integral

$$-\int \frac{r \cdot n}{|r|^3 |r+s|} dS$$

over three spherical surfaces, — a small sphere at $r=0$ and a small sphere at $r=-s$ and a large sphere with the center near the origin; n is the normal on the surfaces from the domain of original volume integral. The integration over the first small spherical surface gives the right-hand side of (4.2), those over the other two vanishing.

Denoting by $c_2 \cos \theta$ and $c_2 \sin \theta$ the parallel and perpendicular components of the electron velocity with respect to the magnetic field, and by ω_2 the gyration frequency of the electron, we have

$$|s(t, c_2)| = c_2 [2(\sin \theta / \omega_2)^2 (1 - \cos \omega_2 t) + t^2 \cos^2 \theta]^{\frac{1}{2}} \quad \text{and}$$

$$\int \frac{1}{|s(t, c_2)|} f_2 dc_2 = 2n_2 \left(\frac{m_2}{2\pi k T_2} \right)^{\frac{1}{2}} \frac{\tanh^{-1} Y}{Y} \frac{1}{|t|} \quad (4.3)$$

where

$$Y \equiv \left[1 - \frac{2(1 - \cos y)}{y^2} \right]^{\frac{1}{2}}, \quad y \equiv \omega_2 t. \quad (4.4)$$

Thus, (2.8) is calculated to be, with R^0 defined by (3.5),

$$R = R^0 \left[\ln(t_p/t_s) + \int_0^{\omega_2 t_p} \left(\frac{\tanh^{-1} Y}{Y} - 1 \right) \frac{dy}{y} \right]; \quad (4.5)$$

the second term in the bracket being an increasing function of $\omega_2 t_p$. The first term $\ln(t_p/t_s)$ give the same result as (3.6).

When the magnetic field is very strong, (4.5) approaches

$$R = R^0 [\ln(t_p/t_s) + \frac{1}{2} (\ln \omega_2 t_p)^2] \quad \text{for } \omega_2 t_p \gg 1, \quad (4.6)$$

or as a limit $R = R^0 \frac{1}{2} (\ln \omega_2 t_p)^2$ which agrees with a result obtained in Part I.

In conclusion, the rate of relaxation increases with increasing magnetic field from

$$R = R^0 \ln(t_p/t_s) \quad \text{for } \omega_2 t_p \leq 1 \quad (4.7)$$

to (4.6). Here $\omega_2 t_p$ is equal to the ratio of the Debye shielding length to the electron gyration radius.

References

- 1) T. Kihara: J. Phys. Soc. Japan **14** (1959) 1751.
- 2) T. Kihara: J. Phys. Soc. Japan **14** (1959) 402.
- 3) R. L. Liboff: Phys. Fluids **2** (1959) 40.

Axially Symmetric Stagnation-point Flow of an Electrically Conducting Fluid under Transverse Magnetic Field

By Tsunehiko KAKUTANI

Department of Physics, Faculty of Science, Kyoto University

(Received December 4, 1959)

This paper deals with the axially symmetric stagnation-point flow of an incompressible, viscous and electrically conducting fluid in the presence of a transverse magnetic field with small magnetic Reynolds numbers. The velocity distribution modified by the magnetic field is calculated for several values of N ($=SR_m$, S : the pressure number, R_m : the magnetic Reynolds number). The shear stress on the wall is expressed in terms of b and $\phi''(0)$, where b is a characteristic parameter of the asymptotic inviscid flow and $\phi''(0)$ is the non-dimensional velocity gradient on the wall.

The flow of this type may be considered as a simple model of the circumstance in the neighbourhood of the nose of a body of revolution moving through an ionized atmosphere at hypersonic speed. In this context, it may be convenient to use Bush's results for estimating b . The ratio of the shear stresses with and without the magnetic field thus calculated is shown graphically as a function of N . It is found that the shear stress at the wall is considerably reduced by the hydromagnetic interactions.

§ 1. Introduction

Recently, Neuringer and McIlroy^{1,2)} and Rossow³⁾ investigated the *two-dimensional* stagnation-point flow of an incompressible, viscous and electrically conducting fluid under a transverse magnetic field in connection with the problem of hypersonic flow past a blunt-nosed body. On the other hand, Bush⁴⁾ studied a magnetohydrodynamic-hypersonic flow of an incompressible, *inviscid* and electrically conducting fluid impinging upon a spherical body in the presence of a magnetic field of dipole type. He extended Lighthill's method⁵⁾, which had been proposed for solving the problem of a dissociating gas, to the magnetohydrodynamical case. He assumed the form of the shock wave as spherical and found that a spherical body surface concentric with the shock wave is possible under a certain critical value of a magnetic parameter ($Q_0=4.2$ in his definition).

In this paper, we attempt to solve the *axially symmetric* stagnation-point flow of an incompressible, *viscous* and electrically conducting fluid in the presence of a transverse uniform magnetic field with small magnetic Reynolds numbers. The velocity field is completely determined if the asymptotic field far from the wall is specified, and the shear

stress on the wall is given in terms of the 'intensity' of the asymptotic field, being characterized by the parameter b .

An interesting application of this result to the problem of hypersonic flow past a blunt-nosed body of revolution may be made in relation to Bush's work.⁴⁾ Looking at the situation of Bush's field described above in the neighbourhood of the stagnation point, we may find that the spherical wall is approximately plane and the magnetic field is essentially uniform and perpendicular to this plane wall. If we take this field as the asymptotic field of the present problem, we can obtain, as the result of the calculation,

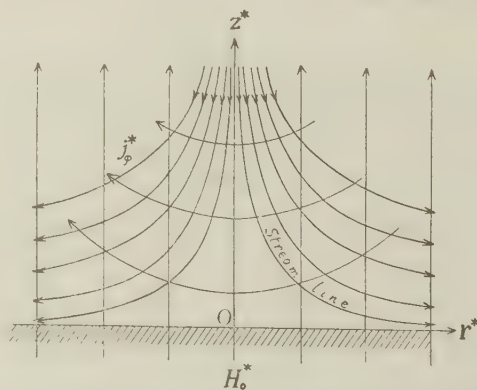


Fig. 1. Sketch of the field.

the information about the fine structure of the flow field in the vicinity of the wall, and, in particular, we shall be able to calculate the change in the shear stress due to the presence of the magnetic field.

It is well known that, in the limit of small magnetic Reynolds numbers, we can neglect the induced magnetic field in comparison with the applied field, that is, the applied magnetic field is essentially undisturbed by the induced electric current. This approximation makes the mathematical analysis considerably simple, and moreover, it is quite realistic in the practical problems of astro-

nautics. Therefore, we are concerned exclusively with this limit throughout the present work.

§ 2. Analysis

Fundamental equations for the velocity $\mathbf{u}$ and the intensity of the magnetic field $\mathbf{H}$ are derived from the equations of motion and Maxwell's equations. They may be written in the non-dimensional form as follows, using cylindrical polar coordinate system (r, φ, z) with the z -axis taken along the axis of symmetry:

$$\left. \begin{aligned} u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} &= -\frac{\partial p}{\partial r} + \frac{1}{Re} \left(\nabla^2 u_r - \frac{u_r}{r^2} \right) + SR_m H_z (u_z H_r - u_r H_z), \\ u_r \frac{\partial u_z}{\partial r} + u_z \frac{\partial u_z}{\partial z} &= -\frac{\partial p}{\partial z} + \frac{1}{Re} \nabla^2 u_z - SR_m H_r (u_z H_r - u_r H_z), \\ \operatorname{div} \mathbf{u} &= \frac{1}{r} \frac{\partial}{\partial r} (r u_r) + \frac{\partial u_z}{\partial z} = 0, \\ \frac{\partial H_r}{\partial z} - \frac{\partial H_z}{\partial r} &= R_m (u_z H_r - u_r H_z), \\ \operatorname{div} \mathbf{H} &= \frac{1}{r} \frac{\partial}{\partial r} (r H_r) + \frac{\partial H_z}{\partial z} = 0, \\ \nabla^2 &\equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}, \end{aligned} \right\} \quad (2.1)$$

with

where the field quantities are made non-dimensional with reference to the characteristic length L_0^* , velocity $U_0^{*†}$ and

$Re = U_0^* L_0^* / \nu$: the Reynolds number,

$R_m = \sigma \mu U_0^* L_0^*$: the magnetic Reynolds number,

$S = \mu H_0^{*2} / \rho U_0^{*2}$: the pressure number,

H_0^* : the intensity of the applied magnetic field,

ν : the coefficient of kinematic viscosity of the fluid,

σ : the conductivity of the fluid,

μ : the permeability of the fluid,

ρ : the density of the fluid.

The rationalized M.K.S. system of unit is used throughout this paper.

The electric field has already been set to be zero in deriving the above equations, since it is easily shown that the electric field $\mathbf{E}$ is identically zero in this axially symmetric case. In fact, since $\operatorname{curl} \mathbf{H}$ has the φ -component alone, $j_r = j_z = 0$. Similarly, $\mathbf{u} \times \mathbf{H}$ has

a component in the φ -direction only. Hence, the combination of Ohm's law and the relation $\mathbf{j} = \operatorname{curl} \mathbf{H}$ gives $E_r = E_z = 0$. Furthermore, $\operatorname{curl} \mathbf{E} = 0$ implies that $\partial E_\varphi / \partial z = 0$ and $\partial(r E_\varphi) / \partial r = 0$, and from the assumption of axisymmetry of the field follows $\partial E_\varphi / \partial \varphi = 0$. Thus, only possible solution for E_φ is $(\text{const})/r$. Requesting the regularity of E_φ over the whole space, we arrive at the conclusion that $\mathbf{E}$ is identically zero.

Now, we assume $\mathbf{u}$, $\mathbf{H}$ and p in the following form:

$$\left. \begin{aligned} u_r &= r \Phi'(z), & u_z &= -2\Phi(z), \\ H_r &= r \Psi'(z), & H_z &= -2\Psi(z), \\ p &= p_0 - p_1(z) - p_2(z)r^2, \end{aligned} \right\} \quad (2.2)$$

so that the conditions $\operatorname{div} \mathbf{u} = 0$ and $\operatorname{div} \mathbf{H} = 0$ in (2.1) are automatically satisfied. Here, the prime denotes differentiation with respect to z , and p_0 denotes the non-dimensional stagnation point pressure. The system of equations (2.1) then reduces to the following set of ordinary differential equations:

[†] Here and hereafter star is used to denote dimensional quantities.

$$\Phi'^2 - 2\Phi\Phi'' = 2p_2 + \frac{\Phi'''}{R_e} - 4SR_m\Psi(\Phi'\Psi - \Phi\Psi'), \quad (2.3)$$

$$4\Phi\Phi' = p_1' - \frac{2}{R_e}\Phi'', \quad (2.4)$$

$$p_2' = 2SR_m\Psi'(\Phi'\Psi - \Phi\Psi'), \quad (2.5)$$

$$\Psi'' = 2R_m(\Phi'\Psi - \Phi\Psi'). \quad (2.6)$$

Next, we must consider the boundary conditions for Eqs. (2.3)~(2.6). We assume that the asymptotic field of the flow, at large distances from the wall, takes the form

$$u_r^* = br^*, \quad u_z^* = -2bz^*, \quad (2.7)$$

where $b(=U_0^*/L_0^*)$ is the characteristic parameter representing the 'intensity' of the asymptotic flow field. This is the simplest universal form of the inviscid stagnation-point flow satisfying both continuity and symmetry conditions. Then, the boundary conditions for the velocity field may be written as

$$\Phi(0) = \Phi'(0) = 0 \text{ and } \Phi'(\infty) \rightarrow 1, \quad (2.8)$$

the former of which implies that the velocity components vanish on the wall and the latter requires that the flow tends to the assumed potential flow at large distances from the wall.

If the wall is an electrical insulator and has the same permeability as the fluid, the magnetic field must be continuous to the applied uniform magnetic field at the wall. Then, we have following boundary conditions for the magnetic field:

$$\Psi(0) = -\frac{1}{2} \text{ and } \Psi'(0) = 0. \quad (2.9)$$

Our problem is thus to find the solution Φ , Ψ , p_1 and p_2 of Eqs. (2.3)~(2.6) which satisfy the boundary conditions (2.8) and (2.9).

We assume here that R_m is very small compared with unity but $SR_m(=N)$ is of order of unity in order to take the hydromagnetic interaction into consideration. We may call this approximation 'the magnetic Stokes approximation' in view of its analogy with the Stokes approximation in ordinary hydrodynamics. This approximation makes mathematical analysis considerably simple, for in

† When R_m is small but not infinitesimal and when z is large, each of $\Phi'\Psi$ and $\Phi\Psi'$ is of $O(z)$. But $(\Phi'\Psi - \Phi\Psi')$ is finite and tends to zero as $z \rightarrow \infty$. Hence, Eq. (2.10) is a good approximation of Eq. (2.6) for all values of z when R_m is sufficiently small.

this limit the magnetic field is solved independently from the flow field. Moreover the assumption of small R_m is quite realistic in most practical problems of astronautics to which the results of the present paper may readily be applied. Using this approximation, Eq. (2.6) is reduced to

$$\Psi'' = 0^{\dagger}. \quad (2.10)$$

Integrating this equation with respect to z and remembering the boundary conditions (2.9), we have

$$\Psi = -\frac{1}{2}, \quad (2.11)$$

which implies that the magnetic field is uniform, to the magnetic Stokes approximation, throughout the whole region. Eq. (2.5) is then reduced to $p_2' = 0$, and hence

$$p_2 = A (= \text{const}). \quad (2.12)$$

Eq. (2.3) then becomes

$$\Phi'^2 - 2\Phi\Phi'' = 2A + \frac{\Phi'''}{R_e} - N\Phi', \quad (2.13)$$

and Eq. (2.4) is used for determining p_1 when Φ is known.

By virtue of the second condition of (2.8), the constant A is found to be $(1+N)/2$. Thus, we arrive at the following equation for Φ :

$$\Phi'^2 - 2\Phi\Phi'' = 1 + N + \frac{\Phi'''}{R_e} - N\Phi', \quad (2.14)$$

subject to the boundary conditions (2.8).

§ 3. Solution of Eq. (2.14)

We introduce here the following variables y and ϕ in place of z and Φ respectively:

$$zR_e^{\frac{1}{2}} = y, \quad \Phi R_e^{\frac{1}{2}} = \phi. \quad (3.1)$$

Eq. (2.14) and the boundary conditions (2.8) then become

$$\phi'^2 - 2\phi\phi'' = 1 + N + \phi''' - N\phi', \quad (3.2)$$

and

$$\phi(0) = \phi'(0) = 0, \quad \phi'(\infty) \rightarrow 1, \quad (3.3)$$

where and hereafter primes denote differentiations with respect to the new variable y .

First, we solve Eq. (3.2) in two separate regions of the flow field, one being the region near the wall and the other far from the wall, and then we connect these two solutions at some suitable point between these two regions.

(i) Inner solution (the solution for small y)
 In the vicinity of the wall, we express the solution in the form

$$\phi=\sum_{n=0}^{\infty}a_ny^n. \tag{3.4}$$

Substituting (3.4) into Eq. (3.2) and equating coefficients of the same powers of y , we obtain a 's as follows:

$$\left. \begin{aligned} a_0 &= 0, \\ a_1 &= 0, \\ a_2 &: \text{to be determined}, \\ a_3 &= -\frac{1}{6}(1+N), \\ a_4 &= \frac{1}{12}Na_2, \\ a_5 &= -\frac{1}{120}N(1+N), \\ a_6 &= \frac{1}{360}(2+2N+N^2)a_2, \\ &\dots\dots\dots \end{aligned} \right\} \tag{3.5}$$

and all of a 's except a_2 are to be determined if a_2 is specified by the analytical continuation with outer solution.

(ii) Outer solution (the asymptotic solution for large y)
 For large values of y , we look for the solution of the form

$$\phi=y+\chi(y), \tag{3.6}$$

where χ represents the small perturbation from the potential solution. Substituting (3.6) into Eq. (3.2) and neglecting higher-order terms with respect to χ , we obtain

$$\chi'''+2y\chi''-(2+N)\chi'=0, \tag{3.7}$$

with the boundary condition

$$\chi'(\infty)\rightarrow 0. \tag{3.8}$$

A solution of Eq. (3.7) satisfying the condition (3.8) is obtained, using Weber's function $D_n(z)$ [†], as follows:

$$\chi=\int_y^{\infty}\exp(-\tfrac{1}{2}y^2)D_{-(2+N/2)}(\sqrt{2}y)dy. \tag{3.9}$$

When n is a negative integer, $D_n(z)$ can be written in the following simple form:

$$\begin{aligned} D_{-(m+1)}(z) &= \exp(\tfrac{1}{4}z^2)\int_z^{\infty}du_0\int_{u_0}^{\infty}du_1\dots \\ &\times \int_{u_{m-1}}^{\infty}du_m\exp(-\tfrac{1}{2}u_m^2), (m+1=-n), \end{aligned}$$

but otherwise the expression of $D_n(z)$ is rather complicated and their numerical values are not given in any existing mathematical tables. In this paper, therefore, the numerical computations are carried out only for the cases of $N=0, 2$ and 4 ($n=-2, -3$ and -4).

After some tedious but straightforward calculations, we obtain the following final expressions of the outer solutions for each value of N .

$$\left. \begin{aligned} \phi(y) &= y + \frac{A_0}{2} \left\{ ye^{-y^2} - (1+2y^2) \int_y^{\infty} e^{-v^2} dy \right\} + B_0 & \text{for } N=0, \\ \phi(y) &= y - \frac{A_2}{3\sqrt{2}} \left\{ (1+y^2)e^{-y^2} - y(3+2y^2) \int_y^{\infty} e^{-v^2} dy \right\} + B_2 & \text{for } N=2, \\ \phi(y) &= y + \frac{A_4}{24} \left\{ y(5+2y^2)e^{-y^2} - (3+12y^2+4y^4) \int_y^{\infty} e^{-v^2} dy \right\} + B_4 & \text{for } N=4, \end{aligned} \right\} \tag{3.10}$$

where A 's and B 's are constants of integration.

(iii) Matching of the solutions

In order to complete the solution over the whole region, we have to join the above two solutions analytically at some appropriate intermediate point, say y_0 , between the two regions. Noting that Eq. (3.2) is of the third order, we may easily see that the analytical continuation of the solution is carried out by making the functional value, the first and the second-order derivatives of the solution continuous at the point y_0 .

We have calculated the inner solution up to the term of a_{15} for each value of N . It is observed that the region of good convergency of the outer solution becomes wider with increasing N , and the contrary situation is found for the inner solution. In practice, we have chosen, as a trial, $y_0=1.5, 1.0$ and 0.8 for $N=0, 2$ and 4 respectively. Matching the above two solutions with each other, the unknown constants a_2, A 's and B 's are determined as follows:

[†] For the definition of $D_n(z)$, see, for example, Morse & Feshbach⁶⁾.

For $N=0$: $a_2=0.660$, $A_0=-2.13$ and $B_0=-0.554^\dagger$,
For $N=2$: $a_2=0.967$, $A_2=-2.24$ and $B_2=-0.426$,
For $N=4$: $a_2=1.20$, $A_4=-3.72$ and $B_4=-0.362$.

}

(3.11)

Eq. (3.2) is thus completely solved and the solution is given by (3.4) and (3.10) together with the numerical values of (3.11). This is the exact solution of the axially symmetric stagnation-point flow of an incompressible, viscous and electrically conducting fluid with small magnetic Reynolds numbers, and the flow field is completely determined if the parameter b is specified.

The non-dimensional velocity profiles ϕ and ϕ' calculated from (3.4) and (3.10) are tabulated in Table I and shown graphically in Fig. 2.

Table I. Non-dimensional velocity profiles for various values of N .

	$N=0$		$N=2$		$N=4$	
y	ϕ	ϕ'	ϕ	ϕ'	ϕ	ϕ'
0	0	0	0	0	0	0
0.2	0.0251	0.244	0.0349	0.332	0.0419	0.392
0.4	0.0949	0.448	0.126	0.570	0.147	0.645
0.6	0.202	0.613	0.258	0.736	0.294	0.805
0.8	0.338	0.742	0.417	0.848	0.465	0.903
1.0	0.496	0.837	0.595	0.921	0.649	0.952
1.2	0.671	0.904	0.783	0.962	0.842	0.979
1.4	0.856	0.949	0.978	0.983	1.04	0.991
1.6	1.05	0.978	1.18	0.993	1.24	0.997
1.8	1.25	0.991	1.37	0.997	1.44	0.999
2.0	1.45	0.996	1.57	0.999	1.64	1.000
2.2	1.65	0.999	1.77	1.000		
2.4	1.85	1.000				

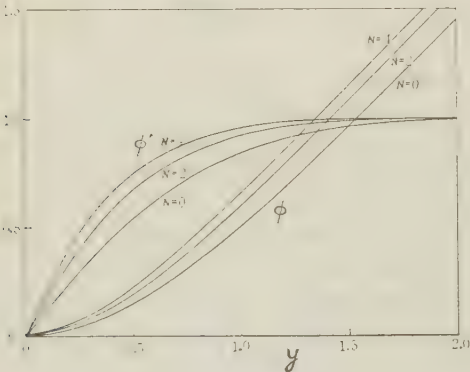


Fig. 2. Non-dimensional velocity profiles *versus* y .

§ 4. Shear Stress

The shear stress, τ , at the wall is given by

$\dagger$ Values of a_2 , A_0 and B_0 for magnetic-free case were given by Homann⁷⁾ taking up to the term of a_{25} for the inner solution and choosing $y_0=1.8$: $a_2=0.658619$, $A_0=-2.16492$ and $B_0=-0.557611$.

$$\tau = \rho \nu \left(\frac{\partial u_r^*}{\partial z^*} \right)_{z^*=0} = \rho \nu \frac{1}{2} r^* b^{3/2} \phi''(0) . \quad (4.1)$$

On the other hand, the drag due to Maxwell's stress is identically zero, since $H_r^*(0)=0$ at the wall which is assumed to be an electrical insulator. Thus, if b , the parameter representing the intensity of the outer flow, is specified by any principle, the total stress is calculated from (4.1).

Now we want to correlate the present problem with Bush's case⁴⁾ in order to apply our result to the problem of hypersonic flow past a blunt-nosed body. Bush investigated the flow field of an inviscid fluid surrounded by the body surface and the detached shock wave preceding it. If we take this flow field as the outer flow of our problem, the present results will give informations about the fine structure of the flow in the 'boundary layer' along the wall and thus the change of the shear stress with the intensity of the magnetic field. In order that Bush's solution for the inviscid fluid may be used as the outer flow of our case, the stand-off distance of the shock wave must be very large in comparison with the thickness of the boundary layer, and this condition is usually satisfied in most practical cases. Another difference between Bush's case and the present one lies in that Bush carried through calculation for finite values of R_m , whereas we assumed here R_m to be infinitesimally small. This difference, however, does not seem essential, because it is concluded in Bush's work that the circumstance does not change appreciably with R_m —especially for the range of the values of magnetic parameter considered in this paper—so far as the values of R_m of about 0.2~1 are concerned^{††}. The same trend was also pointed out by Rossow³⁾ in the case of plane hydromagnetic stagnation-point flow. Rossow showed that the ratio of the shear stresses with and without the magnetic field as calculated by using the magnetic Stokes approximation differs only by 0.25% from

$\dagger\dagger$ R_m defined by Bush is $R_m=\sigma\mu c^*U_\infty^*$, where c^* is the radius of the shock wave and U_∞^* is the uniform speed upstream of the shock wave.

the exact value. Thus it may safely be assumed that the velocity field calculated by Bush for finite values of $R_m (=0.2)$ may be used without modification for the outer field of the present case ($R_m \approx 0$).

Now, if we expand Bush's stream function $f^*(R^*)$ in the neighbourhood of the stagnation-point as

$$f^*(R^*) = \left(\frac{R^* - R_b^*}{R_b^*} \right) f_1^* + \left(\frac{R^* - R_b^*}{R_b^*} \right)^2 f_2^* + \dots, \quad (4.2)$$

where $f_1^*, f_2^*, \dots$ are constants, the velocity components along the R^* - and θ -directions are given by

$$\left. \begin{aligned} u_R^* &= \frac{2 \cos \theta}{R^{*2}} f^*(R^*) \sim \frac{2 f_1^*}{R_b^{*3}} (R^* - R_b^*), \\ u_\theta^* &= -\frac{\sin \theta}{R^*} \frac{df^*(R^*)}{dR^*} \sim -\frac{f_1^*}{R_b^{*3}} R_b^* \theta, \end{aligned} \right\} \quad (4.3)$$

respectively, where R^* is the distance measured from the centre of the spherical body, θ is the angle measured from the axis of symmetry in a meridian plane and R_b^* is the radius of the body. In the neighbourhood of the stagnation-point, $R^* - R_b^*$ and $R_b^* \theta$ may be replaced by z^* and r^* of our problem respectively. Hence, the parameter b in (2.7) must be identical with $-f_1^*/R_b^{*3}$, which in turn is equal to the velocity gradient at the wall: $[(1/R^*)(\partial u_\theta^*/\partial \theta)]_{\text{body}} = U_\infty^* V_s/c^*$ (see Eq. (4.16) of Reference 4), where V_s is the non-dimensional parameter of the velocity gradient at the wall defined by $V_s = (-F'/R^2)_{\text{body}}$, F and R being the non-dimensional forms of f^* and R^* respectively.

Similarly, the R^* -component of Bush's magnetic induction B_R^* on the body surface may be expressed as

$$B_R^* = 2\alpha M(R_b)/R_b^2, \quad (4.4)$$

where α is a constant parameter associated with the intensity of the magnetic induction and $M(R)$ is the non-dimensional 'magnetic stream function'. On the other hand, the θ -component of the magnetic induction B_θ^* is of higher order of θ compared with B_R^* in the vicinity of the stagnation-point. Thus, in the region near the stagnation-point, Bush's magnetic field reduces to a uniform field perpendicular to the wall. Our magnetic parameter is defined as

$$N = SR_m = \frac{\sigma \mu^2 H_0^{*2}}{\rho b}, \quad (4.5)$$

whereas Bush defined his magnetic parameter by

$$Q = \frac{\sigma \alpha^2 c^*}{\rho_\infty U_\infty^{*2}}, \quad (4.6)$$

where ρ_∞ is the density of the fluid upstream of the shock wave. He also introduced the density ratio across the shock wave as

$$\varepsilon = \rho_\infty/\rho, \quad (4.7)$$

whose numerical value was taken 1/11 as a practical value for the hypersonic flight. Comparing (4.5) and (4.6) and remembering that $b = U_\infty^* V_s/c^*$ and $\mu H_0^* = 2\alpha M_b/R_b^2$, we have

$$N = \frac{4\varepsilon M_b^2}{V_s R_b^4} Q. \quad (4.8)$$

Using Eqs. (4.9), (4.15) and (4.17) of Bush's paper,[†] (4.8) becomes, putting $\varepsilon = 1/11$,

$$N \equiv N(Q) = \frac{P(1+\Delta)^2}{11 V_s^2} - 1, \quad (4.9)$$

where P (the non-dimensional parameter of the pressure-relief on the body), Δ (the non-dimensional stand-off distance) and V_s are all given as functions of Q in his paper.

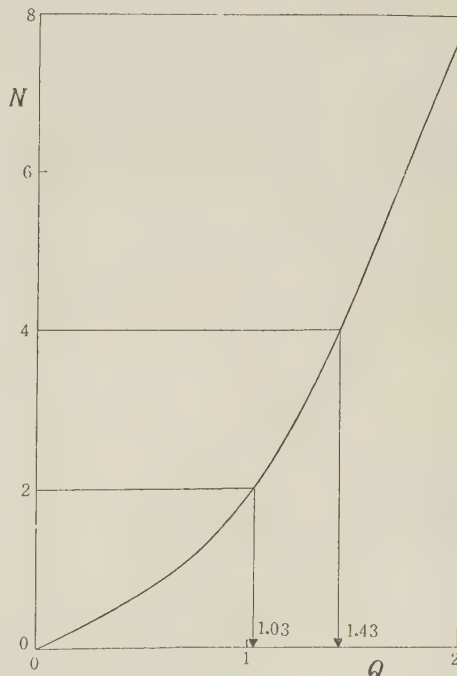


Fig. 3. N versus Q .

[†] (4.9): $\Delta = [(1-R)/R]_{\text{body}}$

(4.15): $P = [11 F'^2/R^2 - 4Q F' M^2/R^4]_{\text{body}}$

(4.17): $V_s = [-F'/R^2]_{\text{body}}$

(see Reference 4)

The relation (4.9) is shown graphically in Fig. 3, from which it will be seen that $N=0, 2$ and 4 correspond to $Q=0, 1.03$ and 1.43 respectively.

Now, from (4.1) the ratio of the shear stresses with and without the magnetic field is given by

$$\frac{\tau}{\tau_0} = \left(\frac{b}{b_0}\right)^{\frac{3}{2}} \frac{\phi''(0)}{\phi_0''(0)}, \tag{4.10}$$

where quantities with suffix o correspond to the non-magnetic case. In this expression, $(b/b_0)^{3/2}$ represents the contribution from the modification of the asymptotic inviscid flow due to the magnetic field, and $\phi''(0)/\phi_0''(0)$ that from the change in the non-dimensional velocity profile of the boundary layer. The latter is calculated from the results of §3, while the former is evaluated using Bush's result. His result gives

$$\frac{b}{b_0} = \frac{V_s}{V_{s,0}} \tag{4.11}$$

as a function of Q (see Tables 1 and 2 in Reference 4), and this is shown graphically in Fig. 4. It is found from Figs. 3 and 4 that $b/b_0=1, 0.599$ and 0.496 for $N=0, 2$ and 4 respectively. Thus, we can calculate the ratio of the shear stresses for the above values of N using (4.10). The graphically result is tabulated in Table II and shown in Fig. 5, together with those calculated using the assumption of Neuringer and McIlroy† for

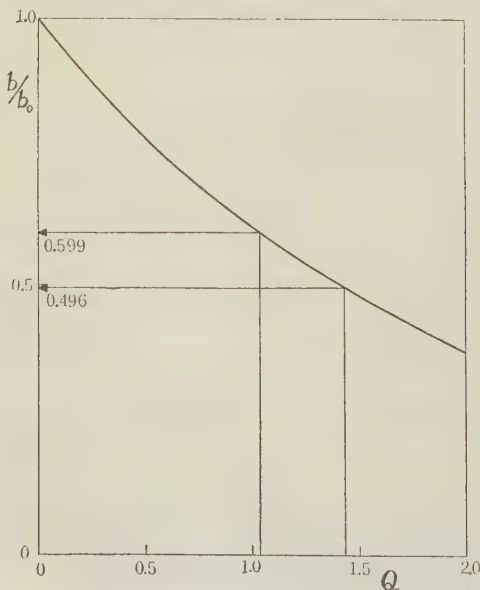


Fig. 4. b/b_0 versus Q .

Table II. Shear stress ratios for various values of N , where $\phi_0''(0)=1.321$.

N	b/b_0	$(b/b_0)^{3/2}$	$\phi''(0)/\phi_0''(0)$	τ/τ_0
calculated using Bush's data				
0	1	1	1	1
2	0.599	0.464	1.463	0.679
4	0.496	0.349	1.812	0.632
calculated from the assumption of Neuringer and McIlroy				
0	1	1	1	1
2	0.577	0.439	1.463	0.642
4	0.447	0.299	1.812	0.542

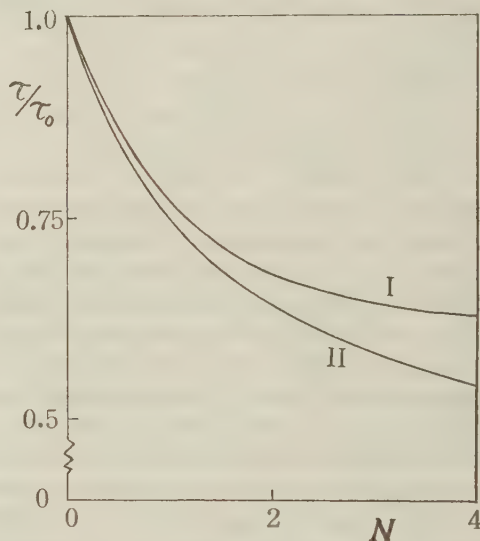


Fig. 5. Shear stress ratio τ/τ_0 versus N .
 Curve I: calculated using Bush's data.
 Curve II: calculated from the assumption of Neuringer and McIlroy.

comparison. It may be seen from Fig. 5, that the reduction of the shear stress with increasing N is not very different from that due to Neuringer and McIlroy's assumption for small values of N .

§ 5. Concluding Discussions

A theoretical investigation of the axially symmetric stagnation-point flow of a conduct-

† Assumeing that the pressure distribution along the wall is unaffected by the presence of the magnetic field, Neuringer and McIlroy¹⁾ obtained $b/b_0=(1+N)^{-1/2}$. Rossow³⁾ also employed this assumption. This seems, however, somewhat arbitrary and unrealistic, since there is a clear evidence for the modification of the pressure relief on the body as just given by Bush⁴⁾.

ing fluid in the presence of an external uniform magnetic field normal to the wall has been carried out for the case of small magnetic Reynolds numbers. The result has been applied to the flow near the nose of a body of revolution flying through an ionized atmosphere at hypersonic speed.

The change of the shear stress at the wall by the hydromagnetic interaction has been calculated using the data of the inviscid flow obtained by Bush⁴⁾. It has been found that the shear stress decreases with increasing N .

The physical mechanism of the hydromagnetic interaction may be considered as such as follows. On the wall, where the fluid is at rest, the induction current is zero. As we go away from the wall the radial velocity component increases, so that the induced electric current also increases. The resulting increase in Lorentz force counteracts the radial flow, and gives rise to the reduction in the radial velocity gradient near the edge of the boundary layer in steady state. This reduction exceeds the counter effect of the increase in the velocity gradient of the boundary layer (see Table II or Fig. 2), thus resulting in the net decrease in the shear stress on the wall. This situation is just represented mathematically by the expression (4.10) of the shear stress ratio; as shown in Table II, the reduction of $(b/b_0)^{3/2}$ exceeds the increase in $\phi''(0)/\phi_0''(0)$. This mechanism is qualitatively similar to that in the two-dimensional case discussed by Neuringer and McIlroy¹⁾.

It may also be expected that the heat-transfer is decreased by applying the magne-

tic field, though no explicit calculation has been attempted in this work.

Our numerical calculation had to be restricted to a few values of the magnetic parameter, N , owing to the lack of the complete table of Weber's function $D_n(z)$. However, the calculation may be easily extended to many other values of N and finite values of R_m , if the high-speed electronic computer would become available.

Acknowledgement

The writer wishes to express his cordial thanks to Prof. S. Tomotika for his continual encouragement. The writer's thanks are also due to Prof. K. Tamada, Dr. T. Tatsumi, Mr. H. Yosinobu and Mr. K. Gotoh for their helpful discussions and suggestions. During the course of this work the writer has been in receipt of a grant-in-aid for fundamental scientific research from the Ministry of Education.

References

- 1) J. L. Neuringer and W. McIlroy: *J. Aero. Sci.* **25** (1958) 194.
- 2) J. L. Neuringer and W. McIlroy: *J. Aero. Sci.* **25** (1958) 332.
- 3) V. J. Rossow: *J. Aero. Sci.* **25** (1958) 334.
- 4) W. B. Bush: *J. Aero. Sci.* **25** (1958) 685.
- 5) M. J. Lighthill: *J. Fluid Mech.* **2** (1957) 1.
- 6) P. M. Morse and H. Feshbach: *Methods of Theoretical Physics* (McGraw-Hill, 1953) Part II, pp. 1403-1405.
- 7) F. Homann: *Z. angew. Math. Mech.* **16** (1936) 153

Stokes Flow of an Electrically Conducting Fluid in a Uniform Magnetic Field

By Kanefusa GOTOH

Department of Physics, Faculty of Science, Kyoto University

(Received December 7, 1959)

The flow of an incompressible, viscous, electrically conducting fluid past an obstacle in a uniform magnetic field is investigated using Stokes approximation. No particular configuration of the flow and the magnetic field is assumed, so that the result applies to the general three-dimensional problems.

§§ 2 and 3 deal with the general theory. It is found that the neutrality of the electric charge density does not hold exactly, when the undisturbed magnetic field is not perpendicular to the vorticity vector. It is also found that the vorticity and the electric current density are confined in a paraboloidal region, thus making a 'wake' which extends in the direction of the undisturbed magnetic field. Distribution of the electric charge density also shows the same structure.

In § 4, the flow past a sphere is investigated as an example. The drag is obtained in a power series of the Hartmann number M . The component of the drag perpendicular to the undisturbed magnetic line of force is found to be larger than its parallel component. It is pointed out as an interesting feature of the three-dimensional cases that the velocity field includes components which express the two-dimensional irrotational flow.

§ 1. Introduction

Recently the problem of the steady flow of an incompressible, viscous, electrically conducting fluid past an obstacle in the presence of a uniform magnetic field has become to attract wider attentions. For the two-dimensional and axisymmetric problems, use of the stream function and the magnetic stream function simplifies analysis considerably, and it is not difficult to carry out the mathematical analysis beyond the lowest approximation (Stokes approximation). In fact, several cases of this kind have been calculated using higher (Oseen) approximation (see Table 1).

On the other hand, we have no such simplifying technique in the general three-dimensional problems and the mathematical analysis becomes necessarily complicated. In this paper an attempt is made to discuss the three-dimensional problems in general.

In §§ 2 and 3, solutions for the velocity and magnetic fields are obtained for a body of arbitrary shape. The results obtained include, of course, the two-dimensional and axisymmetric cases, but in these cases the general approach is not superior to the analysis by use of the stream function. One of the characteristic features of the general three-

dimensional problem, where the magnetic field $\mathbf{H}$ is not always perpendicular to the vorticity vector $\boldsymbol{\omega}$, lies in the fact that the electric charge density is not exactly zero. In other words, the electrical neutrality does not strictly hold, although the charge density is so small that the field is essentially neutral. Along the direction of the undisturbed magnetic field there appears a 'wake'-like region in which the vorticity and the current density have appreciable values. This situation of the field has already been mentioned in the two-dimensional and axisymmetric cases. The distribution of the electric charge density has also a similar structure, that is, the charge is distributed in the 'wake' only.

In the two-dimensional and axisymmetric problems, the velocity field outside the wake is known to be almost uniform. But, it is found that this is not the case in the general three-dimensional field.

In § 4, the flow past a sphere is calculated as an example of the analysis in §§ 2 and 3. The velocity field has components which express a two-dimensional doublet field. The force acting on the sphere is obtained in the form of a power series of the Hartmann number M . The component of the resultant

Table I. Classification of the flows past a body in a uniform magnetic field.

	Direction of flow and magnetic field		Degree of approximation	Body
Two-dimensional field	$\mathbf{H} \cdot \boldsymbol{\omega} = 0$	$(\mathbf{H} \times \mathbf{u})_\infty = 0$	Stokes (Yosinobu and Kakutani) ²⁾	cylinder
			Oseen (Yosinobu) ³⁾	cylinder
		$(\mathbf{H} \times \mathbf{u})_\infty \neq 0$	Stokes (Yosinobu and Kakutani) ²⁾	cylinder
	$\mathbf{H} \cdot \boldsymbol{\omega} \neq 0^\dagger$		discussed in Appendix I in this paper	
Axi-symmetric field	$\mathbf{H} \cdot \boldsymbol{\omega} = 0$		Stokes (Chester) ¹⁾	sphere
			Oseen (Gotoh) ⁴⁾	sphere
Three-dimensional field	no restriction		Stokes (present paper)	sphere

$\dagger$ This case is discussed in the present paper. Prof. K. Tamada pointed out that an exact solution exists in this case, that is, $\mathbf{H}=\text{const.}$, $\mathbf{J}=0$, $\mathbf{E}=\mathbf{u} \times \mathbf{H}$, and the electric charge density $=\nabla \cdot (\mathbf{u} \times \mathbf{H})$, $\mathbf{u}$ and p being obtained from purely hydrodynamical equations. It should be noted that these solutions are independent of the parameters M and R_m .

force perpendicular to the undisturbed magnetic line of force is found, as may be expected, to be greater than its parallel component.

§ 2. Fundamental Equations and Stokes Approximation

The fundamental equations of magneto-hydrodynamics in the steady state are expressed in non-dimensional form as follows: Modified Navier-Stokes equation

$R(\mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \nabla^2 \mathbf{u} + M^2 \mathbf{J} \times \mathbf{H}; \tag{1}$

Equation of continuity

$\nabla \cdot \mathbf{u} = 0; \tag{2}$

Maxwell equations

$\nabla \cdot \mathbf{H} = 0, \tag{3}$

$\nabla \times \mathbf{H} = R_m \mathbf{J}, \tag{4}$

$\nabla \times \mathbf{E} = 0, \tag{5}$

$\nabla \cdot \mathbf{E} = q; \tag{6}$

Ohm's law

$\mathbf{J} = \mathbf{E} + \mathbf{u} \times \mathbf{H}, \tag{7}$

where

- $\mathbf{E}$: the electric field,
- $\mathbf{H}$: the magnetic field,
- $\mathbf{J}$: the electric current density,
- q : the excess charge density,
- $\mathbf{u}$: the fluid velocity,
- p : the pressure;
- $R=aU_\infty/\nu$: the Reynolds number,
- $R_m=4\pi\sigma a\mu U_\infty$: the magnetic Reynolds number,

$M=a\mu H_\infty[\sigma/(\rho\nu)]^{\frac{1}{2}}$: the Hartmann number; all quantities being made non-dimensional with reference to

- U_∞ : the magnitude of the (dimensional) undisturbed velocity,
- H_∞ : the magnitude of the (dimensional) undisturbed magnetic field,
- a : the characteristic length scale of the body,
- ν : the coefficient of kinematic viscosity,
- σ : the electrical conductivity,
- ρ : the fluid density,
- μ : the magnetic permeability.

In the above quantities ν, σ, ρ and μ are

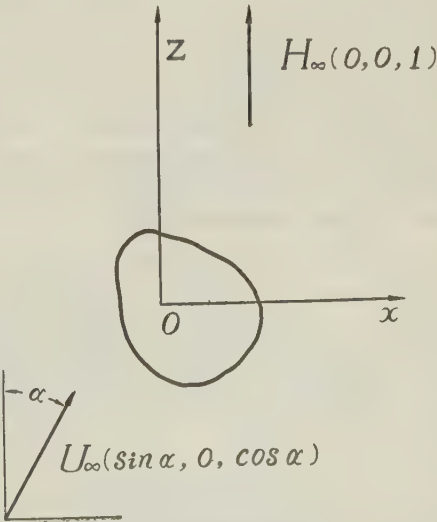


Fig. 1.

assumed to be constant, and all electro-magnetic quantities are measured in electro-magnetic unit. The terms $(\epsilon U_\infty/4\pi\sigma ac^2)qu$ and $(\epsilon U_\infty/4\pi\sigma ac^2)M^2qE$ which should be included in the exact equations have been neglected, since they are of order of $(1/c^2)$ in comparison with other terms, where c is the velocity of light.

Now we take cartesian coordinate system (x, y, z) with the origin at a point inside the body, the z -axis being parallel to the undisturbed magnetic line of force and the x -axis in a plane containing both the z -axis and a straight line parallel to the undisturbed velocity. Then, at great distances from the body, we have asymptotically $H \sim (0, 0, 1)$ and $u \sim (\sin \alpha, 0, \cos \alpha)$, where α denotes the angle between the undisturbed velocity u and magnetic field H (see Fig. 1).

Eq. (5) shows that the electric field E may be expressed in terms of the potential, ϕ , say;

$$E = -\nabla\phi. \quad (8)$$

The electric charge density q is obtained, if necessary, from Eq. (6).

Here we confine ourselves to slow motions at small values of the Reynolds number R and employ Stokes approximation to the velocity field. Neglecting the term containing R in Eq. (1) and eliminating J from this equation and Eq. (7), we obtain

$$\nabla^2 u + M^2(E + u \times H) \times H = \nabla p. \quad (9)$$

In many practical problems, $1/\nu$ is much larger than $\sigma\mu$, so that small R gives small magnetic Reynolds number R_m , and we shall assume here this is the case. When the term containing R_m is neglected in Eq. (4) (this procedure may be referred to as 'Stokes approximation' with respect to R_m in view of its analogy with Stokes approximation for slow motions in ordinary hydrodynamics), we obtain the undisturbed solution

$$H = (0, 0, 1), \quad (10)$$

provided both the fluid and the body are non-magnetic and their permeabilities are effectively equal to each other. Substituting this result into Eq. (9), we have the following scalar equations:

$$\Delta u_x - M^2 \left(\frac{\partial \phi}{\partial y} + u_x \right) = \frac{\partial p}{\partial x}, \quad (11)$$

$$\Delta u_y + M^2 \left(\frac{\partial \phi}{\partial x} - u_y \right) = \frac{\partial p}{\partial y}, \quad (12)$$

$$\Delta u_z = \frac{\partial p}{\partial z}, \quad (13)$$

where $\Delta \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

Divergence of Eq. (4) gives the equation of continuity for the electric current density J :

$$\nabla \cdot J = 0. \quad (14)$$

Eliminating J from this equation and Ohm's law (7), we have the following relationship between u , H and ϕ :

$$\nabla^2 \phi - H(\nabla \times u) - R_m u \cdot \nabla \phi = 0. \quad (15)$$

If, according to the magnetic Stokes approximation, we neglect the term containing R_m , this equation reduces to

$$\nabla^2 \phi - H(\nabla \times u) = 0. \quad (16)$$

Eqs. (11)~(13) and (16), together with Eq. (2), furnish us with the sufficient equations for calculating the field quantities u , p and ϕ .

The electric field within the body is determined by solving the potential equation:

$$\Delta \phi^{(b)} = 0. \quad (17)$$

The electric charge density may be expressed, using (16), as

$$q = \nabla \cdot E = -H(\nabla \times u), \quad (18)$$

and its right-hand side does not generally vanish. In all cases so far investigated, the right-hand side of (18) vanished exactly thanks to the presence of some symmetry in the velocity and magnetic fields, and the electric neutrality of the field has been taken as a matter of course. In this general case, however, we have no reason to assume the right-hand side of Eq. (18) to vanish, and, in fact, the example described in §4 will show that the electric charge really appears in the flow field past a sphere. As already mentioned, we have neglected the terms containing q in deriving Eqs. (1) and (7). It may be said, therefore, that we are treating the field as electrically 'neutral' in spite of the appearance of the charge density q .

§ 3. General Solutions and their Properties

General solutions of Eqs. (2), (11)~(13) and (16) may be expressed in the following forms

† In the exact analysis the relation between u , H and E may be derived more easily by eliminating J between Eqs. (4) and (7), but in the present approximation we cannot follow this procedure because the term $R_m J$ is neglected in Eq. (4).

$$u_x = \frac{\partial}{\partial x} [P^{(1)} + P^{(2)}] + \frac{\partial}{\partial y} [\phi^{(1)} + \phi^{(2)}] + f_0, \quad (19)$$

$$u_y = \frac{\partial}{\partial y} [P^{(1)} + P^{(2)}] - \frac{\partial}{\partial x} [\phi^{(1)} + \phi^{(2)}], \quad (20)$$

$$u_z = \frac{\partial}{\partial z} [P^{(1)} + P^{(2)}] - M[P^{(1)} - P^{(2)}], \quad (21)$$

$$\phi = \frac{1}{M} \frac{\partial}{\partial z} [\phi^{(1)} - \phi^{(2)}] - [\phi^{(1)} + \phi^{(2)}] - f_0 y, \quad (22)$$

$$p = M \frac{\partial}{\partial z} [P^{(1)} - P^{(2)}] - M^2 [P^{(1)} + P^{(2)}], \quad (23)$$

where f_0 is an arbitrary constant and $P^{(1)}$, $P^{(2)}$, $\phi^{(1)}$ and $\phi^{(2)}$ are respectively the solutions of the following equations

$$\left(\Delta - M \frac{\partial}{\partial z} \right) P^{(1)} = 0, \quad \left(\Delta + M \frac{\partial}{\partial z} \right) P^{(2)} = 0, \quad (24)$$

$$\left(\Delta - M \frac{\partial}{\partial z} \right) \phi^{(1)} = 0, \quad \left(\Delta + M \frac{\partial}{\partial z} \right) \phi^{(2)} = 0. \quad (25)$$

Here we should note that the solutions $P^{(1)}$, $P^{(2)}$, $\phi^{(1)}$ and $\phi^{(2)}$ are not always regular functions of the coordinates, whereas we require the regularity for u , ϕ and p .

If we employ the polar coordinate system (r, θ, φ) with the line $\theta=0$ in the direction of the undisturbed magnetic field, the solutions of Eqs. (24) and (25) are generally expressed as:

$$\begin{aligned} \begin{pmatrix} P^{(1)} \\ \phi^{(1)} \end{pmatrix} = \sum_{n,\lambda} \begin{pmatrix} A_{n\lambda} \cos \lambda \varphi + A_{n\lambda}^* \sin \lambda \varphi \\ C_{n\lambda}^* \cos \lambda \varphi + C_{n\lambda} \sin \lambda \varphi \end{pmatrix} \times \\ \times P_n^\lambda(\mu) \frac{e^{mz}}{\sqrt{mr}} K_{n+1/2}(mr) + \begin{pmatrix} g_1(x, y) \\ g_3(x, y) \end{pmatrix}, \end{aligned} \quad (26)$$

$$\begin{aligned} \begin{pmatrix} P^{(2)} \\ \phi^{(2)} \end{pmatrix} = \sum_{n,\lambda} \begin{pmatrix} B_{n\lambda} \cos \lambda \varphi + B_{n\lambda}^* \sin \lambda \varphi \\ D_{n\lambda}^* \cos \lambda \varphi + D_{n\lambda} \sin \lambda \varphi \end{pmatrix} \times \\ \times P_n^\lambda(\mu) \frac{e^{-mz}}{\sqrt{mr}} K_{n+1/2}(mr) + \begin{pmatrix} g_2(x, y) \\ g_4(x, y) \end{pmatrix}, \end{aligned} \quad (27)$$

where $K_{n+1/2}(mr)$ denotes the modified Bessel function, $P_n^\lambda(\mu)$ the associated Legendre function and g_i 's are the solutions of the two-dimensional potential equation:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) g_i = 0 \quad (28)$$

and $A_{n\lambda}$, $B_{n\lambda}$, $C_{n\lambda}$, $D_{n\lambda}$, $A_{n\lambda}^*$, $B_{n\lambda}^*$, $C_{n\lambda}^*$ and $D_{n\lambda}^*$ are arbitrary constants which will be determined by the boundary conditions and $m=M/2$. If $n \geq \lambda$, P_n^λ are regular for all values of μ , but for $n < \lambda$ they have singularities at $|\mu|=1$. Some of these singularities are cancelled out with each other, but the remaining singularities must be compensated with those of $g_i(x, y)$ ($i=1, 2, 3$ and 4) at $x=y=0$ ($|\mu|=1$). It will be shown in Appendix II that $g_1=g_2=0$.

Now that we have obtained the expressions of u and ϕ in terms of $P^{(l)}$ and $\phi^{(l)}$ ($l=1, 2$), the similar expressions for the current density J , the vorticity $\omega (= \nabla \times u)$ and the charge density q may be derived using (7) and (18):

$$\begin{aligned} J_x &= -\frac{1}{M} \left[\frac{\partial^2}{\partial x \partial z} (\phi^{(1)} - \phi^{(2)}) - M \frac{\partial}{\partial y} (P^{(1)} + P^{(2)}) \right], \\ J_y &= -\frac{1}{M} \left[\frac{\partial^2}{\partial y \partial z} (\phi^{(1)} - \phi^{(2)}) + M \frac{\partial}{\partial x} (P^{(1)} + P^{(2)}) \right], \\ J_z &= -\frac{1}{M} \left[\frac{\partial^2}{\partial z^2} (\phi^{(1)} - \phi^{(2)}) - M \frac{\partial}{\partial z} (\phi^{(1)} + \phi^{(2)}) \right]; \end{aligned} \quad (29)$$

$$u_x = \frac{\partial^2}{\partial x \partial z} (\phi^{(1)} + \phi^{(2)}) - M \frac{\partial}{\partial y} (P^{(1)} - P^{(2)}),$$

$$u_y = \frac{\partial^2}{\partial y \partial z} (\phi^{(1)} + \phi^{(2)}) + M \frac{\partial}{\partial x} (P^{(1)} - P^{(2)}), \quad (30)$$

$$u_z = \frac{\partial^2}{\partial z^2} (\phi^{(1)} + \phi^{(2)}) - M \frac{\partial}{\partial z} (\phi^{(1)} - \phi^{(2)});$$

$$q = M \frac{\partial}{\partial z} (\phi^{(1)} - \phi^{(2)}) - \frac{\partial^2}{\partial z^2} (\phi^{(1)} + \phi^{(2)}). \quad (31)$$

Since $g_1=g_2=0$ and g_3 and g_4 are independent of z , all g_i 's do not appear in Eqs. (29), (30) and (31). For large values of r , we have asymptotically

$$\frac{1}{\sqrt{mr}} K_{n+1/2}(mr) \sim \sqrt{\frac{\pi}{2}} \frac{1}{mr} e^{-mr},$$

and it follows that

$$\begin{pmatrix} P^{(1)} \\ \phi^{(1)} \end{pmatrix} \propto e^{-mr(1-\cos\theta)} = e^{-2mr \sin^2(\theta/2)},$$

$$\begin{pmatrix} P^{(2)} \\ \phi^{(2)} \end{pmatrix} \propto e^{-mr(1+\cos\theta)} = e^{-2mr \sin^2[(\pi-\theta)/2]},$$

these asymptotic behaviours of $P^{(l)}$ and $\phi^{(l)}$ clearly show that the above quantities J , ω and q become vanishingly small for large r except for two regions bounded by the surfaces $r \sin^2 \theta = \text{const}$ and $r \sin^2 (\pi - \theta) = \text{const}$. These regions take the shape of two paraboloids extending on both sides of the body in the direction of the undisturbed magnetic field, and may be referred to as the 'wake' in view of its parallelism with the wake in ordinary hydrodynamics.

These features of the distributions of the vorticity and the current density are quite similar to those in the two-dimensional and axisymmetric cases. Unlike in these two cases, however, the flow outside the wake is not uniform in the present case, owing to the presence of two-dimensional solutions g_3 and g_4 which do not vanish outside the wake like

other three-dimensional solutions. This situation will be illustrated in the next section.

The solution of Eq. (17), which is regular within the body, is given as follows:

$$\phi^{(b)} = \sum_{n=0}^{\infty} [G_{n\lambda} \sin \lambda \varphi + G_{n\lambda}^* \cos \lambda \varphi] P_n^{\lambda}(\mu) r^n, \quad (32)$$

where G 's are arbitrary constants.

§ 4. Flow past a Sphere

Now we investigate, as an example, the flow past a sphere in a uniform magnetic field. Since the fundamental equations are linearized in our method of approximation, the general field may be constructed by the linear combination of two simpler fields, one in which the main stream is parallel to the uniform magnetic field and the other in which they are perpendicular to each other. The former case was already solved by Chester,¹⁾ so that we need only to consider the latter.

For convenience the characteristic velocity is taken, instead of U_{∞} , as $U_0 = U_{\infty}/[1+f(m)]$, where $f(m)$ is an unknown function which will be determined by the boundary conditions, and the radius of the sphere is taken as the characteristic length a .

The boundary conditions for the velocity field are the same as those in ordinary hydrodynamics, namely, the velocity becomes uniform at great distances from the body and it must vanish on the surface of body:

$$\mathbf{u} = (\sin \alpha, 0, \cos \alpha) \text{ at infinity}, \quad (33)$$

$$\mathbf{u} = 0 \quad \text{on the surface of body.} \quad (34)$$

The boundary conditions for the electromagnetic field are that both the tangential component of the electric field and the normal component of the current density are continuous at the solid boundary, and the electric field becomes uniform at infinity (there $\mathbf{H} = \text{const}$, so that $\mathbf{J} = 0$ and $\mathbf{E} = \mathbf{H} \times \mathbf{u}$). Thus we have, as the boundary conditions,

$$\frac{\partial \phi}{\partial y} = -\sin \alpha, \quad \frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial z} = 0 \text{ at infinity}, \quad (35)$$

$$(\mathbf{t} \cdot \nabla) \phi = (\mathbf{t} \cdot \nabla) \phi^{(b)}, \quad \left. \begin{array}{l} \sigma_f (\mathbf{n} \cdot \nabla) \phi - \sigma_b (\mathbf{n} \cdot \nabla) \phi^{(b)}, \\ \varepsilon_f (\mathbf{n} \cdot \nabla) \phi - \varepsilon_b (\mathbf{n} \cdot \nabla) \phi^{(b)} = -\tilde{\omega}, \end{array} \right\} \begin{array}{l} \text{on the} \\ \text{surface} \\ \text{of body,} \end{array} \quad (36)$$

$$\sigma_f (\mathbf{n} \cdot \nabla) \phi - \sigma_b (\mathbf{n} \cdot \nabla) \phi^{(b)}, \quad (37)$$

$$\varepsilon_f (\mathbf{n} \cdot \nabla) \phi - \varepsilon_b (\mathbf{n} \cdot \nabla) \phi^{(b)} = -\tilde{\omega}, \quad (38)$$

where $\mathbf{n}$ and $\mathbf{t}$ are unit vectors in the direc-

tions of the normal and tangent to the body surface respectively, $\phi^{(b)}$ denotes the electric potential within the body, $\tilde{\omega}$ the surface density of the electric charge, ε the dielectric constant, and the subscripts f and b represent quantities associated with the fluid and the body respectively. The last condition (38), which comes from $\nabla \cdot \mathbf{E} = q$, is used only to calculate the distribution of the surface density of the electric charge in terms of known data concerning the electric potential.

The solutions in the present example are given by Eqs. (19)~(27). The boundary conditions at infinity requires that f_0 in those expressions must be taken as $[1+f(m)] \sin \alpha$, and due to the symmetry of the sphere the arbitrary constants with asterisk all vanish and others do so too, unless $\lambda=1$, so that their second suffices are omitted hereafter. Concerning the singular terms ($n=0$) we must replace

$$A_0 P_0^1 \text{ by } A_0 \sqrt{\frac{1-\mu}{1+\mu}} \text{ in } P^{(1)},$$

$$B_0 P_0^1 \text{ by } B_0 \sqrt{\frac{1+\mu}{1-\mu}} \text{ in } P^{(2)},$$

$$C_0 P_0^1 \text{ by } A_0 \sqrt{\frac{1-\mu}{1+\mu}} + C_0 \sqrt{\frac{1+\mu}{1-\mu}} \text{ in } \phi^{(1)},$$

$$D_0 P_0^1 \text{ by } B_0 \sqrt{\frac{1+\mu}{1-\mu}} + C_0 \sqrt{\frac{1-\mu}{1+\mu}} \text{ in } \phi^{(2)},$$

respectively and the two-dimensional solutions g_l ($l=3, 4$) are

$$g_3 = g_4 = -C_0 \sqrt{\frac{\pi}{2}} \frac{\sin \varphi}{\sqrt{1-\mu^2} mr}.$$

These terms represent the potential due to the two-dimensional doublet. In contrast with the contributions from other terms, this doublet potential does not vanish even outside the wake, thus giving rise to a field structure similar to the plane potential flow past a cylindrical body. This fact may not be entirely unexpected in view of the strong influence of the magnetic line of force, and this is in fact one of the interesting features of the general three-dimensional case.

The arbitrary constants A_n, B_n, C_n, D_n and G_n are determined by imposing the boundary conditions (34), (36) and (37) on the solutions (19)~(22) and (32), and we have

$$\begin{aligned} [u_\rho]_{r=1} &= [\cos \varphi u_x + \sin \varphi u_y]_{r=1} \\ &= \left[(1+f) \sin \alpha \cos \varphi + \sqrt{1-\mu^2} \left(\frac{\partial}{\partial r} - \frac{\mu}{r} \frac{\partial}{\partial \mu} \right) (P^{(1)} + P^{(2)}) + \frac{1}{r \sqrt{1-\mu^2}} \frac{\partial}{\partial \varphi} (\phi^{(1)} + \phi^{(2)}) \right]_{r=1} \end{aligned}$$

$$\begin{aligned}
&= \sum_{l=1}^{\infty} \left[(1+f) \sin \alpha \delta_{l1} - C_0 e^{mr} R_0 m r \gamma_{l-1} \right. \\
&\quad + \{A_0 + (-1)^{1+l} B_0\} \left\{ (R_0 - m r R_1) X_{l,1} + \frac{1}{3} m r R_1 X_{l,2} \right\} \\
&\quad - \sum_{n=1}^{\infty} \{A_n + (-1)^{n+l} B_n\} \left\{ X_{l,n} R_n + \frac{n(n+1)}{2n+1} m r (\phi_{l,n-1} R_{n-1} - \phi_{l,n+1} R_{n+1}) \right\} \\
&\quad \left. + \sum_{n=1}^{\infty} \{C_n + (-1)^{n+l} D_n\} X_{l,n} R_n \right]_{r=1} \cos \varphi P_l' = 0, \quad (39)
\end{aligned}$$

$$[u_\varphi]_{r=1} = [\cos \varphi u_y - \sin \varphi u_x]_{r=1}$$

$$\begin{aligned}
&= \left[-(1+f) \sin \alpha \sin \varphi + \frac{1}{r \sqrt{1-\mu^2}} \frac{\partial}{\partial \varphi} (P^{(1)} + P^{(2)}) - \sqrt{1-\mu^2} \left(\frac{\partial}{\partial r} - \frac{\mu}{r} \frac{\partial}{\partial \mu} \right) (\phi^{(1)} + \phi^{(2)}) \right]_{r=1} \\
&= - \sum_{l=1}^{\infty} \left[(1+f) \sin \alpha \delta_{l1} + \{A_0 + (-1)^{1+l} B_0\} \left\{ (R_0 - m r R_1) X_{l,1} + \frac{1}{3} m r R_1 X_{l,2} \right\} \right. \\
&\quad + C_0 \left\{ 2 e^{mr} R_0 \delta_{l1} - m r R_1 [1 + (-1)^{1+l}] \left[X_{l,1} + \frac{1}{3} X_{l,2} \right] - e^{mr} R_0 \beta_{l-1} \right\} \\
&\quad - \sum_{n=1}^{\infty} \{C_n + (-1)^{n+l} D_n\} \left\{ X_{l,n} R_n + \frac{n(n+1)}{2n+1} m r (\phi_{l,n-1} R_{n-1} - \phi_{l,n+1} R_{n+1}) \right\} \\
&\quad \left. + \sum_{n=1}^{\infty} \{A_n + (-1)^{n+l} B_n\} X_{l,n} R_n \right]_{r=1} \sin \varphi P_l' = 0, \quad (40)
\end{aligned}$$

$$\begin{aligned}
[u_z]_{r=1} &= -m \sum_{l=1}^{\infty} \left[\{A_0 + (-1)^l B_0\} R_1 X_{l,1} \right. \\
&\quad \left. + \sum_{n=1}^{\infty} \{A_n + (-1)^{l+n+l} B_n\} \left\{ X_{l,n} R_n + \frac{n+1}{2n+1} X_{l,n-1} R_{n-1} + \frac{n}{2n+1} X_{l,n+1} R_{n+1} \right\} \right]_{r=1} \cos \varphi P_l' = 0, \quad (41)
\end{aligned}$$

$$\begin{aligned}
[\phi - \phi^{(b)}]_{r=1} &= \sum_{l=1}^{\infty} \left[-r(1+f) \sin \alpha \delta_{l1} + \frac{1}{2} \{A_0 + (-1)^{1+l} B_0\} X_{l,1} R_1 \right. \\
&\quad + C_0 \left\{ e^{mr} m r R_0 \gamma_{l-1} + \frac{1}{2} [1 + (-1)^{1+l}] X_{l,1} R_1 \right\} \\
&\quad - \sum_{n=1}^{\infty} \frac{1}{2} \{C_n + (-1)^{l+n} D_n\} \left\{ X_{l,n} R_n + \frac{n+1}{2n+1} X_{l,n-1} R_{n-1} + \frac{n}{2n+1} X_{l,n+1} R_{n+1} \right\} \\
&\quad \left. - r^l G_l \right]_{r=1} \sin \varphi P_l' = 0, \quad (42)
\end{aligned}$$

$$\begin{aligned}
\left[\frac{\partial \phi}{\partial r} - \frac{\sigma_b}{\sigma_f} \frac{\partial \phi^{(b)}}{\partial r} \right] &= \sum_{l=1}^{\infty} \frac{d}{dr} \left[-r(1+f) \sin \alpha \delta_{l1} - \frac{1}{2} \{A_0 + (-1)^{1+l} B_0\} X_{l,1} R_1 \right. \\
&\quad + C_0 \left\{ e^{mr} m r R_0 \gamma_{l-1} + \frac{1}{2} [1 + (-1)^{1+l}] X_{l,1} R_1 \right\} \\
&\quad - \sum_{n=1}^{\infty} \frac{1}{2} \{C_n + (-1)^{n+l} D_n\} \left\{ X_{l,n} R_n + \frac{n+1}{2n+1} X_{l,n-1} R_{n-1} + \frac{n}{2n+1} X_{l,n+1} R_{n+1} \right\} \\
&\quad \left. - \frac{\sigma_b}{\sigma_f} r^l G_l \right]_{r=1} \sin \varphi P_l' = 0, \quad (43)
\end{aligned}$$

where

$$r_{2\lambda}(mr) = \begin{cases} \frac{3}{mr} \left[1 - e^{-mr} \left(\phi_0 + \frac{1}{3} \phi_1 \right) \right] & \text{for } \lambda=0, \\ e^{-mr} \left[\frac{2}{(2\lambda+1)(4\lambda+1)} \phi_{2\lambda} + \frac{1}{(2\lambda+1)(\lambda+1)} \phi_{2\lambda+1} + \frac{1}{(\lambda+1)(4\lambda+5)} \phi_{2\lambda+2} \right] & \text{for } \lambda \geq 1; \end{cases}$$

$$\beta_{2\lambda}(mr) = \begin{cases} 2 - 2e^{-mr}X_{1,1} - m\gamma_0 & \text{for } \lambda=0, \\ -2e^{-mr}X_{2\lambda+1,1} - m\gamma_{2\lambda} & \text{for } \lambda \geq 1; \end{cases}$$

$$\delta_{\lambda l} = \begin{cases} 1 & \text{for } \lambda=l, \\ 0 & \text{for } \lambda \neq l; \end{cases}$$

$$R_n(mr) = \frac{1}{\sqrt{mr}} K_{n+1/2}(mr),$$

and ϕ_λ , $X_{l,n}$ and $\phi_{l,n}$ are functions of the argument mr alone. It may easily be seen from (39)~(43) that

$$B_0 = A_0; \quad B_n = (-1)^{n+1}A_n,$$

$$D_n = (-1)^{n+1}C_n, \quad G_{2n} = 0 \quad \text{for } n \geq 1,$$

and

$$(1+f)\sin\alpha\delta_{\lambda 0} - C_0 e^m R_0 m \gamma_{2\lambda} + 2A_0 \left\{ (R_0 - mR_1)X_{2\lambda+1,1} + \frac{1}{3}mR_1 X_{2\lambda+1,2} \right\}$$

$$- 2 \sum_{n=1}^{\infty} A_n \left\{ X_{2\lambda+1,n} R_n + \frac{n(n+1)}{2n+1} m (\phi_{2\lambda+1,n-1} R_{n-1} - \phi_{2\lambda+1,n+1} R_{n+1}) \right\}$$

$$+ 2 \sum_{n=1}^{\infty} C_n X_{2\lambda+1,n} R_n = 0 \quad \text{for } \lambda \geq 0, \quad (44)$$

$$(1+f)\sin\alpha\delta_{\lambda 0} + 2A_0 \left\{ (R_0 - mR_1)X_{2\lambda+1,1} + \frac{1}{3}mR_1 X_{2\lambda+1,2} \right\}$$

$$+ C_0 \left\{ 2e^m R_0 \delta_{\lambda 0} - 2mR_1 \left(X_{2\lambda+1,1} + \frac{1}{3}X_{2\lambda+1,2} \right) - e^m R_0 \beta_{2\lambda} \right\}$$

$$- 2 \sum_{n=1}^{\infty} C_n \left\{ X_{2\lambda+1,n} R_n + \frac{n(n+1)}{2n+1} m (\phi_{2\lambda+1,n-1} R_{n-1} - \phi_{2\lambda+1,n+1} R_{n+1}) \right\}$$

$$+ 2 \sum_{n=1}^{\infty} A_n X_{2\lambda+1,n} R_n = 0 \quad \text{for } \lambda \geq 0, \quad (45)$$

$$A_0 X_{2\lambda,1} R_1 + \sum_{n=1}^{\infty} A_n \left\{ X_{2\lambda,n} R_n + \frac{n+1}{2n+1} X_{2\lambda,n-1} R_{n-1} + \frac{n}{2n+1} X_{2\lambda,n+1} R_{n+1} \right\} = 0 \quad \text{for } \lambda \geq 1. \quad (46)$$

Eliminating G_n from (42) and (43), we have the following equations:

$$\left[\left\{ (2\lambda+1) \frac{\sigma_b}{\sigma_f} - \frac{d}{dr} \right\} \left\{ r(1+f)\sin\alpha\delta_{\lambda 0} - C_0 R_0 m r e^{mr} \gamma_{2\lambda} + (A_0 - C_0) X_{2\lambda+1,1} R_1 \right. \right.$$

$$\left. \left. + \sum_{n=1}^{\infty} C_n \left(X_{2\lambda+1,n} R_n + \frac{n+1}{2n+1} X_{2\lambda+1,n-1} R_{n-1} + \frac{n}{2n+1} X_{2\lambda+1,n+1} R_{n+1} \right) \right\} \right]_{r=1} = 0 \quad \text{for } \lambda \geq 0, \quad (47)$$

where the functions $X_{l,n}$ and $\phi_{l,n}$ are defined as the coefficients of the following expansions†

$$e^{m\mu} P_n'(\mu) = \sum_{l=1}^{\infty} X_{l,n}(m) P_l'(\mu),$$

† These functions may be obtained by the following recurrence formulae (see reference 5):

$$(n-1)X_{l,n} = (2n-1)X'_{l,n-1} - nX'_{l,n-2}, \quad X_{l,0} = 0, \quad X_{l,1} = \phi_l/m; \quad (i)$$

$$\phi_{l,n} = (\Psi_{l,n} - X_{l,n})/m, \quad n\Psi_{l,n} = (2n-1)\Psi'_{l,n-1} - (n-1)\Psi_{l,n-2},$$

$$\Psi_{l,0} = \phi_l, \quad \Psi_{l,1} = \frac{l}{2l-1}\phi_{l-1} + \frac{l+1}{2l+3}\phi_{l+1}; \quad (ii)$$

$$\phi_l(m) = (2l+1) \sqrt{\frac{\pi}{2m}} I_{l+1/2}(m), \quad (iii)$$

where $I_n(m)$ is the modified Bessel function of order n , and primes represent differentiation with respect to m .

$$e^{m\mu}P_n(\mu)=\sum_{l=1}^{\infty}\Phi_{l,n}(m)P_l'(\mu).$$

Since it is difficult to solve in general the system of simultaneous equations (44)~(47), we consider the special case of small m . In such a case we obtain

$$\begin{aligned} A_0 &= \frac{3}{8}\sqrt{\frac{2}{\pi}}\left(1+\frac{9}{8}m\right)\sin\alpha+O(m^2), \\ A_1 &= -\frac{m^2}{8}\sqrt{\frac{2}{\pi}}\left(1+\frac{9}{8}m\right)\sin\alpha+O(m^4), \\ A_n &= O(m^{2n}) \quad \text{for } n>1, \\ C_0 &= \frac{3}{8}\sqrt{\frac{2}{\pi}}\left(1+\frac{9}{8}m\right)\sin\alpha+O(m^2), \\ C_n &= O(m^{2n+2}) \quad \text{for } n\geq 1, \\ f(m) &= O(m^2). \end{aligned} \tag{48}$$

The force $\mathbf{F}$ experienced by the body is composed of two parts: one due to the viscous stress exerted by the surrounding fluid on the body surface and the other Lorentz force. These forces are expressed as the integrals on the right-hand side of the following equation

$$\mathbf{F} = -a\rho\nu U_0 \iint_S \{p\mathbf{n} + (\mathbf{n} \times \boldsymbol{\omega})\} dS + a\rho\nu U_0 M^2 \frac{\sigma_0}{\sigma_f} \iiint_V \mathbf{J} \times \mathbf{H} dV, \tag{49}$$

where the first surface integral is taken over the surface of the body and the second volume integral within the body. The former due to the viscous stress is formally identical with that in ordinary hydrodynamics, while the latter due to Lorentz force may be reduced to

$$\iiint_V \mathbf{J} \times \mathbf{H} dV = \left(-\iiint_V \frac{\partial \Phi^{(v)}}{\partial y} dV, \iiint_V \frac{\partial \Phi^{(v)}}{\partial x} dV, 0 \right), \tag{50}$$

using the relations $\mathbf{J} = \mathbf{E} = -\nabla\Phi^{(v)}$ and $\mathbf{H} = (0, 0, 1)$.

If we substitute the solutions (32) and (19)~(27), together with (48), into Eq. (49), we obtain the components of the drag for the case in which the undisturbed velocity is perpendicular to the undisturbed magnetic field. Thus,

$$\begin{aligned} F_x &= 6\pi a\rho\nu U_\infty \sin\alpha \left\{ 1 + \frac{9}{16}M + O(M^2) \right\}, \\ F_y &= F_z = 0. \end{aligned} \tag{51}$$

From these results it will be seen that the conductivity of the sphere does not affect the drag up to the order of M . For the case in which the undisturbed velocity and magnetic field are parallel to each other, the following formulae for the drag were obtained by Chester¹⁾

$$\begin{aligned} F_x &= F_y = 0, \\ F_z &= 6\pi a\rho\nu U_\infty \cos\alpha \left\{ 1 + \frac{3}{8}M + O(M^2) \right\}. \end{aligned} \tag{52}$$

Combining the results (51) and (52) for the parallel and perpendicular cases together, we find that the forces acting on the sphere in the general case are given by

$$\left. \begin{aligned} F_x &= 6\pi a\rho\nu U_\infty \sin\alpha \left\{ 1 + \frac{9}{16}M + O(M^2) \right\}, \\ F_y &= 0, \\ F_z &= 6\pi a\rho\nu U_\infty \cos\alpha \left\{ 1 + \frac{3}{8}M + O(M^2) \right\}. \end{aligned} \right\} \tag{53}$$

It may be interesting to note that the contribution of the magnetic field to the component F_x perpendicular to the magnetic field is, up to the order M , slightly larger than that to the parallel component F_z .

Acknowledgements

The writer wishes to express his cordial thanks to Professor S. Tomotika for his encouragement throughout this work. His thanks are also due to Professor I. Imai, Professor K. Tamada and Dr. T. Tatsumi for their helpful discussions.

Appendix I. Discussions on the Two-dimensional Problem

We discuss briefly the two-dimensional problem, i.e., the flow past a cylinder in a uniform magnetic field parallel to its axis. Introducing the stream function ψ :

$$u_x = -\frac{\partial \psi}{\partial y}, \quad u_y = \frac{\partial \psi}{\partial x},$$

we find from Eq. (16) that ϕ is expressed as:

$$\phi = \psi + \psi^*,$$

where ψ^* is the solution of the homogeneous equation $\Delta \psi^* = 0$. The boundary conditions at infinity (corresponding to (33) and (35)) may be written as

$$\psi = -y, \quad \phi = -y \quad \text{at infinity},$$

and therefore

$$\psi^* = 0 \quad \text{at infinity.} \quad (\text{I-1})$$

On the surface of the cylinder, the conditions for the electric field (36) and (37) requires that

$$(\mathbf{t} \cdot \nabla) (\psi + \psi^*) = (\mathbf{t} \cdot \nabla) \phi^{(b)}, \quad (\text{I-2})$$

$$\sigma_s (\mathbf{n} \cdot \nabla) (\psi + \psi^*) = \sigma_s (\mathbf{n} \cdot \nabla) \phi^{(b)}. \quad (\text{I-3})$$

On the other hand, the conditions for the velocity are

$$(\mathbf{t} \cdot \nabla) \psi = 0, \quad (\mathbf{n} \cdot \nabla) \psi = 0,$$

so that the conditions (I-2) and (I-3) reduce respectively to

$$(\mathbf{t} \cdot \nabla) \psi^* = (\mathbf{t} \cdot \nabla) \phi^{(b)},$$

$$\sigma_s \mathbf{n} \cdot \nabla \psi^* = \sigma_s (\mathbf{n} \cdot \nabla) \phi^{(b)},$$

and these equations generally have no other solution than the trivial ones: $\psi^* \equiv 0$ and $\phi^{(b)} \equiv 0$. From this follows that $\phi = \psi$, giving the vanishing of the coefficients of M^2 in Eqs. (11) and (12). This means that there is no interaction between the velocity and the electro-magnetic fields, and therefore the velocity field may be solved separately in the

same manner as for the non-conducting fluid. (Note that this fact holds generally without using Stokes approximation with respect to R .)† It is well known in ordinary hydrodynamics that Stokes equation $\nabla^2 \psi = 0$ permits no such solution that satisfies boundary conditions at infinity, and in order to obtain such a solution we have to resort to Oseen approximation (in which we neglect, in the equations of motion, the higher order terms of the deviations of the velocity from the undisturbed one, and not of the velocity itself). The same situation may be expected for the velocity field in the present problem, and we have to employ at least Oseen approximation in order to obtain the solution for the velocity field. But we shall not proceed to detailed discussion of this case, since the typical velocity fields of this type have already been investigated by several authors.

Appendix II. Discussions on the Two-dimensional Solutions

Regularity of the physical quantities u_x and p requires that each of the right-hand sides of the following expressions must also be regular:

$$u_x = \frac{\partial}{\partial z} [P^{(1)} - P^{(2)}] - M [P^{(1)} - P^{(2)}], \quad (\text{II-1})$$

$$\frac{1}{M} p = \frac{\partial}{\partial z} [P^{(1)} - P^{(2)}] - M [P^{(1)} + P^{(2)}]. \quad (\text{II-2})$$

Functions $P^{(1)}$ and $P^{(2)}$ as given by (26) and (27) may be rewritten as:

$$P^{(1)} = \sum_{\lambda} \left[\left\{ \sum_n A_{n\lambda} e^{mz} P_n^{\lambda} \frac{1}{\sqrt{mr}} K_{n+1/2} + g_{1\lambda} \right\} \cos \lambda \varphi \right. \\ \left. - \left\{ \sum_n A_{n\lambda}^* e^{-mz} P_n^{\lambda} \frac{1}{\sqrt{mr}} K_{n+1/2} + g_{1\lambda}^* \right\} \sin \lambda \varphi \right], \quad (\text{II-3})$$

$$P^{(2)} = \sum_{\lambda} \left[\left\{ \sum_n B_{n\lambda} e^{-mz} P_n^{\lambda} \frac{1}{\sqrt{mr}} K_{n+1/2} + g_{2\lambda} \right\} \cos \lambda \varphi \right. \\ \left. + \left\{ \sum_n B_{n\lambda}^* e^{-mz} P_n^{\lambda} \frac{1}{\sqrt{mr}} K_{n+1/2} + g_{2\lambda}^* \right\} \sin \lambda \varphi \right]. \quad (\text{II-4})$$

If we substitute these expressions in (II-1) and (II-2) and add them, we see that each of the following quantities must be regular, since $\sin \lambda \varphi$ and $\cos \lambda \varphi$ ($\lambda = 1, 2, \dots$) are independent of each other,

† Prof. K. Tamada pointed out that this is valid not only for small R_m (Stokes approximation) but also for any values of R_m .

$$\left(\frac{\partial}{\partial z} - M\right) \sum_n A_{n\lambda} e^{mz} P_n^\lambda \frac{1}{\sqrt{mr}} K_{n+1/2} - M g_{1\lambda}, \quad \sqrt{\frac{\pi}{2}} \frac{1}{mr} \lim_{\mu \rightarrow 1} \sum_n \bar{A}_{n\lambda} F_{n\lambda} \left[1 + O\left(\frac{1}{mr}\right)\right], \quad (\text{II-10})$$

(II-5) and when $\mu \rightarrow -1$, it becomes

$$\left(\frac{\partial}{\partial z} - M\right) \sum_n A_{n\lambda}^* e^{mz} P_n^\lambda \frac{1}{\sqrt{mr}} K_{n+1/2} - M g_{1\lambda}^*, \quad \sqrt{\frac{\pi}{2}} \frac{1}{mr} e^{-2mr} \lim_{\mu \rightarrow -1} \sum_n \bar{A}_{n\lambda} F_{n\lambda} \left[1 + O\left(\frac{1}{mr}\right)\right]. \quad (\text{II-11})$$

Carrying out the differentiation, we obtain, for example,

$$\begin{aligned} & \left(\frac{\partial}{\partial z} - M\right) \sum_n A_{n\lambda} e^{mz} P_n^\lambda \frac{1}{\sqrt{mr}} K_{n+1/2} \\ &= \frac{1}{\sqrt{mr}} e^{mz} \sum_n \bar{A}_{n\lambda} K_{n+1/2} F_{n\lambda}, \end{aligned} \quad (\text{II-7})$$

where $\bar{A}_{n\lambda}$'s are certain constants and $F_{n\lambda}$ the functions of μ alone. For large values of r , we have

$$\frac{1}{\sqrt{mr}} K_{n+1/2} \sim \sqrt{\frac{\pi}{2}} \frac{1}{mr} e^{-mr} \left[1 + O\left(\frac{1}{mr}\right)\right], \quad (\text{II-8})$$

so that the above quantities may be expressed as:

$$\sqrt{\frac{\pi}{2}} \frac{1}{mr} e^{mz-mr} \sum_n \bar{A}_{n\lambda} F_{n\lambda} \left[1 + O\left(\frac{1}{mr}\right)\right]. \quad (\text{II-9})$$

When $\mu \rightarrow 1$, this quantity approaches to

These quantities cannot be equal for their different dependence on r , that is, the singular part of (II-7) cannot be even function of z , while $g_{1\lambda}$'s, being independent of z , are even functions of z . Hence, the two terms in (II-5) must separately be regular: that is,

$$g_{1\lambda} \equiv 0. \quad (\text{II-12})$$

Similar deduction also gives

$$g_{1\lambda}^* = g_{2\lambda} = g_{2\lambda}^* = 0. \quad (\text{II-13})$$

References

- 1) W. Chester: J. Fluid Mech. **3** (1957) 304.
- 2) H. Yosinobu and T. Kakutani: J. Phys. Soc. Japan **14** (1959) 1433.
- 3) H. Yosinobu: J. Phys. Soc. Japan **15** (1960) 175.
- 4) K. Gotoh: J. Phys. Soc. Japan **15** (1960) 189.
- 5) S. Goldstein: Proc. Roy. Soc. A **123** (1929) 225.

An Investigation of Psychrometer, II

By Yoshirô ÔMORI*

Teikoku Rayon Co. Ltd., Osaka

(Received September 30, 1959)

Experiments have been carried out to determine precisely the psychrometer constant A for dry and humid air in the temperature range of $0\sim 40^\circ\text{C}$. The results were compared with a theoretical formula derived by the present writer by the use of the analogy between the transfers of heat and mass by which A is represented to be proportional to $(C_p\rho D/K)^n$. Experimental values of A are found to be about 4% larger than the theoretical value obtained by taking, as usual, $n=0.3$. The deviation is minute, but better agreement can be obtained by adopting the value of 0.5 for n .

Experiments have also been carried out to examine effects on A of various factors such as atmospheric pressure, size of a psychrometer, ventilation and conditions of supercooling or freezing of wet-bulbs, obtaining good agreement with the theory.

§ 1. Introduction

The so-called 'psychrometer constant' is an important constant in the formula of psychrometer, and efforts have been made by many investigators to determine its value both theoretically and experimentally. Since, however, those experiments are likely to be accompanied by various errors, the results are hardly reliable. So, it is quite necessary to determine the value of the constant by performing more accurate experiments. In a previous paper¹⁾ Kawata and the present writer have carried out experiments on thermocouple psychrometers and examined necessary conditions for exact psychrometry. Based upon these experiences, the writer has intended, in the present work, to obtain experimentally the exact value of the psychrometer constant by eliminating or minimizing various errors occurring in the measurements and applying appropriate corrections to observed values. At the same time, he has tried to find theoretically the value of the constant by applying the theory of analogy between the transfers of heat and mass, using most reliable experimental data about the heat transfer.

§ 2. Derivation of the Formula of Psychrometer

The formula of psychrometer can be deriv-

ed by the use of thermal equilibrium of a wet-bulb, considering that the heat transferred to the wet-bulb from the surrounding air is equal to the latent heat lost by evaporation of water from the bulb. The heat transferred to the wet-bulb, Q , consists of three parts: namely, (1) the heat transferred by conduction and convection from the surrounding air, Q_a ; (2) the heat transferred by conduction through the stem of the wet-bulb thermometer, Q_c ; (3) the heat transferred by radiation from the surroundings, Q_r . Since all these quantities may be considered to be proportional to the difference of dry- and wet-bulb temperatures, we have

$$Q = Q_a + Q_c + Q_r = (\kappa_a + \kappa_c + \kappa_r)(\theta - \theta'_m), \quad (1)$$

where θ and θ'_m are the temperatures of the dry- and wet-bulbs respectively, and κ_a , κ_c and κ_r are constants.

On the other hand, the heat lost by evaporation, Q' , may be put as

$$Q' = LW, \quad (2)$$

where L is the latent heat of vaporization of water and W is the quantity of evaporated water. Since, however, W will be proportional to the difference of the concentrations of water vapor at the wet surface and in the surrounding air, Eq. (2) may be written as

$$W = \gamma(c_{m'} - c), \quad (3)$$

where $c_{m'}$ is the concentration of saturated water vapor corresponding to the temperature of the wet-bulb, c the concentration of water vapor in the air in question, and γ a con-

* The present experiments were performed when the writer was an Assistant Professor of Kyoto University at the Department of Applied Physics, Faculty of Engineering.

stant.

Equating Q and Q' , we have

$$c = c_{m'} - \frac{1}{L} \frac{\kappa_a}{\gamma} \left(1 + \frac{\kappa_o}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) (\theta - \theta'_m). \quad (4)$$

The constants κ_a , κ_o , κ_r and γ depend upon various conditions including the size and shape of the wet-bulb and the ventilation. However, the ratio κ_a/γ is almost unaffected by such conditions and has an important theoretical significance. It is very difficult to determine this ratio completely theoretically, but it is possible to find it semi-empirically by the use of the theory of analogy between the transfers of heat and mass, as well as related experimental results on which comparatively advanced study has been made.

Now, if we consider evaporation from unit area of the surface of a wet-bulb in unit time, κ_a will be the coefficient of heat transfer, the value of which has been obtained theoretically by Pohlhausen²⁾ in the case of a plate placed parallel to a uniform flow and by King³⁾ in the case of a circular cylinder. However, the writer has adopted an empirical formula⁴⁾ worked out by McAdams for a circular cylinder placed perpendicularly to a uniform flow, namely:

$$\frac{\kappa_a d}{K} = \left\{ 0.35 + 0.47 \left(\frac{v \rho d}{\eta} \right)^{0.52} \right\} \left(\frac{C_p \eta}{K} \right)^{0.3}, \quad (5)$$

where d is the diameter of the cylinder, K the thermal conductivity of the fluid (air), C_p the specific heat at constant pressure of the fluid, η the coefficient of viscosity of the fluid, v the fluid velocity and ρ the density of the fluid. All quantities are measured in C. G. S. units.

For various constants of the air, mean values at temperatures of the surface of a wet-bulb and of the surrounding air may be assumed.

By the theory of analogy between the transfers of heat and mass, we have, in the case of evaporation,

$$\frac{r d}{D} = \left\{ 0.35 + 0.47 \left(\frac{v \rho d}{\eta} \right)^{0.52} \right\} \left(\frac{\eta}{\rho D} \right)^{0.3}, \quad (6)$$

where D is the coefficient of diffusion of water vapor and air.

Combining (5) with (6) we have

$$\frac{\kappa_a}{\gamma} = \frac{K}{D} \left(\frac{C_p \eta}{K} / \frac{\eta}{\rho D} \right)^{0.3} = \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3}, \quad (7)$$

where $C_p \eta / K$ is Prandtl number of the air and $\eta / \rho D$ is Schmidt number between the air and

water vapor, and (4) may be written as:

$$c = c_{m'} - \frac{1}{L} \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \left(1 + \frac{\kappa_o}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) \times (\theta - \theta'_m). \quad (8)$$

So far we have considered the case of a circular cylinder placed perpendicularly to air stream. Since, however, it may be assumed that the exponent to $C_p \rho D / K$ in the above formula will not vary sensibly with the shape of a body immersed in air stream, κ_a / γ is taken to be a number expressed by physical constants only. Of these constants ρ , C_p , K and D will take approximately mean values at temperatures of dry- and wet-bulbs, and L a value at the temperature of wet-bulb, and therefore they will alter more or less according to the degree of dependence upon temperature or atmospheric pressure. The factors κ_o / κ_a and κ_r / κ_a change fairly widely subject to conditions of application, so that it is necessary to estimate their magnitudes or to eliminate these quantities by adequate means in practical psychrometry.

While the above psychrometer formula (8) is expressed with the concentration of water vapor, the vapor pressure is used in the usual formula as:

$$p = p_{m'} - AP(\theta - \theta'_m), \quad (9)$$

where p is the water vapor pressure in question, $p_{m'}$ the saturation water vapor pressure at θ'_m , P the atmospheric pressure and A the so-called 'psychrometer constant'.

Therefore, the formula (8) will be rewritten in a form analogous to (9), taking the vapor pressure in place of the concentration of vapor by the use of the relation:

$$c = S \frac{p}{P} \rho_\theta, \quad c_{m'} = S \frac{p_{m'}}{P} \rho_{\theta m'}, \quad (10)$$

where S is the specific weight of water vapor referred to air, ρ_θ the density of dry air at temperature θ and atmospheric pressure P , and $\rho_{\theta m'}$ the density of dry air at temperature θ'_m and atmospheric pressure P .

Thus we obtain

$$p \rho_\theta = p_{m'} \rho_{\theta m'} - \frac{P}{LS} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \times \left(1 + \frac{\kappa_o}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) (\theta - \theta'_m), \quad (11)$$

which may also be written as:

$$p = p_{m'} - \frac{P}{\rho_{\theta} L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \left(1 + \frac{\kappa_c}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) \\ \times (\theta - \theta'_m) + \left(\frac{\rho_{\theta m'}}{\rho_{\theta}} - 1 \right) p_{m'}, \tag{12}$$

while the constant A in (9) is represented by

$$A = \frac{1}{\rho_{\theta} L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \left(1 + \frac{\kappa_c}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) \\ - \frac{1}{\theta - \theta'_m} \left(\frac{\rho_{\theta m'}}{\rho_{\theta}} - 1 \right) \frac{p_{m'}}{P}. \tag{13}$$

The second term on the right-hand side of (13) is an additional term caused by the conversion. Owing to this additional term, therefore, the psychrometer formula undergoes more complicated changes with conditions of temperature and humidity, when the vapor pressure is used. In the present experiments it was considered to be more convenient to represent A graphically against the air temperature, taking the relative humidity as a parameter, so that the writer has adopted the following formulae (12a) and (13a) which are numerically identical with (12) and (13) respectively:

$$p = p_{m'} - \frac{P}{\rho_{\theta m'} L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \left(1 + \frac{\kappa_c}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) \\ \times (\theta - \theta'_m) + \left(1 - \frac{\rho_{\theta}}{\rho_{\theta m'}} \right) p, \tag{12a}$$

and

$$A = \frac{1}{\rho_{\theta m'} L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} \left(1 + \frac{\kappa_c}{\kappa_a} + \frac{\kappa_r}{\kappa_a} \right) \\ - \frac{1}{\theta - \theta'_m} \left(1 - \frac{\rho_{\theta}}{\rho_{\theta m'}} \right) \frac{p}{P}. \tag{13a}$$

Since the second terms in these formulae disappear in the case of dry air, these formulae are very favourable to the present experiments where the complete dryness was taken as the standard state.

§ 3. Numerical Calculations by the Theoretical Formulae

Numerical calculations were carried out by putting reliable values of the physical constants of air and water vapor into the formulae derived in the preceding paragraph. The annexed table shows these physical constants. The value of D was obtained by M. Trautz and W. Müller from the experimental data of Winkelmann, and may be considered to be the most reliable. Since, however, accurate measurements of D are very difficult, there is a fear that the errors involved may be larger than those of other physical constants. It is given as a function of temperature as⁵⁾:

$$D = (0.219 \pm 0.001) \left(\frac{T}{273} \right)^{1.853},$$

where T means the absolute temperature. For K , measurements of which are difficult next to those of D , the value obtained by Weber for dry air has been adopted⁶⁾, namely:

$$K = 5.68 \times 10^{-5} (1 + 0.00365 \theta).$$

It is to be regretted that the writer was compelled to use the values of dry air for ρ , C_p and K , and did not take the thermal diffusion into account. For the temperature upon which these quantities depend, the mean temperature of dry- and wet-bulbs was taken approximately. But, since it is necessary to know the wet-bulb temperature beforehand, it was calculated by Sprung's formula. To get a more exact value it may be advisable to make successive approximations, but there will be no need to do so. In the course of derivation of the theoretical formula, terms of radiation and thermal conduction were not considered.

Table. Physical constants of air and water-vapor adopted for the calculation of A .

+ temp °C +	ρ gr·cm ⁻³	C_p cal·gr ⁻¹ ·°C ⁻¹	K cal·cm ⁻¹ ·sec ⁻¹ ·°C ⁻¹	D cm ² ·sec ⁻¹	L cal·gr ⁻¹
-10	1.342 × 10 ⁻³	0.240	5.47 × 10 ⁻⁵	0.204	599.7 (679.4) *
0	1.293	"	5.68	0.219	595.1 (674.8) *
10	1.247	"	5.89	0.234	590.2
20	1.205	"	6.10	0.250	585.2
30	1.165	"	6.31	0.265	579.6
40	1.128	"	6.51	0.285	574.7

(*)*: Latent heat of sublimation of ice.

(a) *Ratio of the coefficients of transfers of heat and mass*

Calculation of the ratio κ_a/γ by the formula (7) shows that, when the mean of dry- and wet-bulb temperatures lies in ordinary temperature range (say, $0\sim 40^\circ\text{C}$), κ_a/γ will be approximately linear with the mean temperature such that

$$\kappa_a/\gamma = 2.73 \times 10^{-4} (1 - 2.73 \times 10^{-3} \theta_m). \quad (14)$$

(b) *Psychrometer constant A*

The psychrometer constant A is given by

$$A = \frac{1}{\rho_{\theta_m} L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3} - \frac{1}{\theta - \theta_m} \left(1 - \frac{\rho_{\theta}}{\rho_{\theta_m}} \right) \frac{p}{P}. \quad (13b)$$

Thus A changes with temperature and humidity, and if we take the dry-bulb temperature as abscissa and the relative humidity as a parameter, it is represented as shown in Fig. 1, and also if we take the relative humidity as abscissa and the dry-bulb temperature as a parameter, A is represented as shown in Fig. 2. The latter representation is more convenient to represent A which is obtained for humid air in the experiments described later.

As seen from these figures, the constant A takes a nearly constant value, 5.6×10^{-4} , in dry or slightly humid conditions, uut, owing to

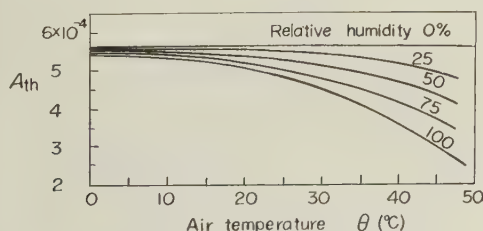


Fig. 1. Relation between theoretical A and air temperature.

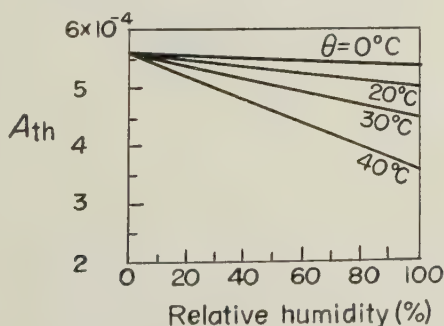


Fig. 2. Relation between theoretical A and relative humidity.

the effect of the additional term due to the conversion, it decreases when humidity becomes higher. Considering this point, it is advisable, for measurements to require high accuracy, to get humidity by, for example, Sprung's formula, as a first approximation, and use the value of A corresponding to the humidity.

(c) *Value of A when the wet-bulb is frozen*

In the preceding case (b) a wet-bulb was covered with water. When the temperature of a wet-bulb is below 0°C , water may be supercooled or frozen, and the temperature of the bulb as well as the constant A will take different values according to the condition in which the wet-bulb lies. Under the condition of such a low temperature and low humidity it is sufficient to take only the first term for A . Since the temperature of a wet-bulb is not different considerably in either case of freezing and supercooling, the difference of A may be ascribed to the difference of L in the two cases, if we take the temperature upon which the physical constants concerned depend to be equal in both cases. Therefore, the ratio of the values of A in the two cases will be

$$\frac{A \text{ (freezing)}}{A \text{ (supercooling)}} = \frac{\text{heat of vaporization of water}}{\text{heat of sublimation of ice}} = 0.883,$$

the respective value of A being

$$A \text{ (supercooling)} = 5.60 \times 10^{-4}, \text{ and}$$

$$A \text{ (freezing)} = 4.95 \times 10^{-4},$$

when θ_m is about -6°C . Thus, when a wet-bulb temperature is below 0°C , care should be taken to ascertain whether the bulb is frozen or supercooled before the formula is applied.

(d) *Influence of change of atmospheric pressure*

Since the factors appearing in the formula for A will be affected directly or indirectly by the atmospheric pressure, it is necessary to study to what degree the constant A is varied by the atmospheric pressure. When only the first term is taken into account, we have

$$A = \frac{1}{\rho L S} \cdot \frac{K}{D} \left(\frac{C_p \rho D}{K} \right)^{0.3}.$$

For many practical purposes we may assume

only the normal atmospheric pressure. Then, since S is constant and C_p , L and K are all very nearly independent of the pressure according to both theory and experiment, we have

$$A \propto (\rho D)^{-0.7},$$

so far as the pressure is concerned. However, it is known that D is inversely proportional to ρ so that the constant A may be considered to be independent of the atmospheric pressure.

§ 4. Apparatuses for Measuring A

The apparatuses for measuring A include psychrometers, thermocouples and mercury-in-glass thermometers, a test chamber of constant temperature and humidity, electrical measuring instruments, etc.

(a) *Psychrometers and temperature measuring apparatuses*

Thermocouple psychrometers were adopted whose properties have been investigated in detail. They have several favorable points for the present purpose in comparison with mercury-in-glass thermometers, namely, (1) a test chamber needs only a small scale; (2) exact temperature measurements are possible; and especially (3) it is easy to exclude conduction of heat through the stem and also the correction for radiation can be calculated easily. The thermocouple consisted of wires of chromel and constantan of 0.2 mm. For the measurements of wet-bulb temperature, two junctions corresponding to dry- and wet-bulbs were connected differentially and butt-jointed with silver solder. One of the junctions was left bare and was taken as a dry-bulb, while the other junction taken as a wet-bulb was covered with a white cotton thread, washed in alcohol and in boiling water, and moistened with a small quantity of distilled water, about 8 cm in length along thermocouple wires. Dry-bulb temperature was measured with another thermocouple and also with a mercury-in-glass thermometer graduated to 0.1° . Calibrations of the thermocouple thermometers and mercury-in-glass thermometers were performed with a mercury-in-glass thermometer tested at the Central Inspection Institute of Weights and Measures to an accuracy of $\pm 0.03^\circ\text{C}$. The electromotive forces were measured with two precision type potentiometers of Yokogawa

Seisakusho and Shimazu Seisakusho combined with sensitive mirror galvanometers of R type B class and M type E class of Shimazu Seisakusho. Figs. 3 and 4 show two psychrometers employed in the present experiments. The reason why two psychrometers were used is for ascertaining reproducibility of the measurements and also for convenience of periodical calibration. They were used alternately and equivalently, showing no difference in results. Fig. 5 shows a wet-junction covered with moistened cloth of cotton thread.

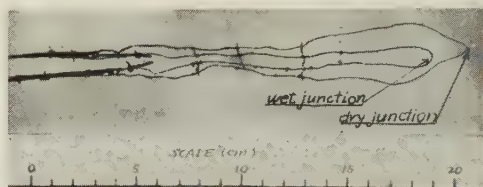


Fig. 3. Thermocouple psychrometer No. 1 used for determining A .

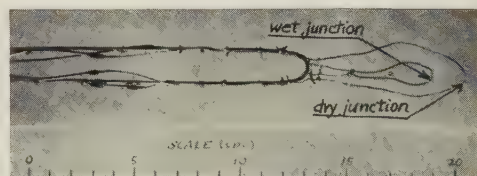


Fig. 4. Thermocouple psychrometer No. 2 used for determining A .



Fig. 5. Wet-junction covered with thread.

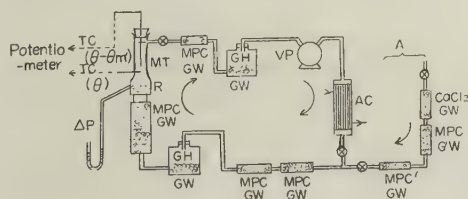
(b) *Apparatuses for testing psychrometers* (i) *Chamber of constant temperature and constant humidity*

A chamber of constant temperature and constant humidity was constructed in order to perform measurements under various temperatures and humidities. At first it was intended to keep a large water-filled bath at

any desired constant temperature by means of a sensitive thermostat. In effect, it was able to keep the temperature within $\pm 0.01^\circ\text{C}$ with regard to both locality and time by sufficient stirring of water and careful thermal insulation. A cubical chamber with side of 30 cm long was put in this water bath. The chamber was made of 4 mm thick brass plates welded at each edge, its air-tightness having been examined by vacuum test. Many beakers filled with sulphuric acid of prescribed concentration were put in the chamber and the air in it was stirred with a propeller. Again, the chamber was provided with a lid for taking the beakers in and out, and with pipes for inserting psychrometers, thermometers, anemometers, stirrers, etc. Special care was taken so that outside air or moisture might not enter the chamber through crevices. Since the interior of the chamber was connected to the outer atmosphere by a long capillary tube, the pressure there was kept equal to the atmospheric pressure.

(ii) Apparatus for circulating dry air

The equipment described in (i) admits to perform experiments under any desired conditions of temperature and humidity, but it has a drawback that there is a fear that humidity may increase gradually. In order to ensure higher accuracy of measurements, therefore, a contrivance was made by which dry air was applied continuously upon a psychrometer. Fig. 6 shows a schematic diagram of the apparatus.



- MT : Tube for measurement
- GH : Gas holder
- VP : Vacuum pump
- AC : Air cooler
- R : Part to decrease turbulence of flow
- TC : Thermocouple
- MPC: $\text{Mg}(\text{ClO}_4)_2$
- GW : Glass wool
- ΔP : U-tube manometer
- A : Part to decrease pressure drop

Fig. 6. Schematic diagram of dry air circulating apparatus.

Air was circulated by a rotary vacuum pump. In the path of circulation a plentiful drying agent of $\text{Mg}(\text{ClO}_4)_2$ soaked into asbestos was filled, which is very excellent in various points including a large capacity of absorbing moisture and very low equilibrium vapor pressure. Air pressure in the chamber was estimated by measuring pressure difference from atmospheric pressure with a mercury manometer. Also, the correction for radiation was made by measuring wind velocity at the position of insertion of the psychrometer. The temperature in the circulation tube was measured with a thermocouple, but, since the temperature would somewhat rise by the circulation of air, it was contrived to make the temperature as close to the room temperature as possible by inserting a heat exchanger in the way.

§ 5. Outline of the Experiments

In determining psychrometer constant A from indications of dry- and wet-bulb temperatures, it is necessary in principle to know correct temperature and humidity, and technically to have large drop of wet-bulb temperature from dry-bulb temperature. For these requirements it is most advantageous to use perfectly dry air. Therefore, chief measurements have been performed in extremely dry state desiccated with very concentrated sulphuric acid or $\text{Mg}(\text{ClO}_4)_2$. By this procedure, the apparent psychrometer constant, A_{app} , as given by

$$A_{\text{app}} = \frac{p_m'}{P(\theta - \theta'_m)}$$

was first obtained by direct measurement, and then, by making correction for radiation, the real constant which will be denoted by A_{obs} was found. Before describing details of the experiments, the method of calculating the correction for radiation will be given.

As mentioned before, in addition to the correction for radiation the correction must be made for the conduction of heat through the stem of a thermometer. Partial drying of a moistened cloth of a wet-bulb should also be considered. However, the effect of the former may be excluded by making adequately long wet-covering¹⁾, and it seems unnecessary to take account of the latter except in a special case as will be described later where freezing occurs. This may be said with suf-

ficient confidence from the fact that wet-bulb temperature has remained very nearly constant with time in the case of circulating air.

The correction term due to radiation, κ_r/κ_a , may be obtained as follows. κ_a can be calculated as a function of the diameter of wet-bulb and the wind velocity by using McAdams' equation for circular cylinders. In the present case the diameter of the wet-bulb was about 1 mm and the wind velocity varied in the range of 60~150 cm/sec. κ_r may be calculated from the exchange of radiant heat. In the case of a small wet-bulb placed in a large at space surrounded by a wall at the dry-bulb temperature. Thus the quantity of heat received in unit time by unit area of the surface of the wet-bulb is given by

$$Q_r = \varepsilon_w \sigma (T^4 - T_m^4) \doteq 4 \varepsilon_w \sigma T_M^3 (\theta - \theta_m'), \quad (14)$$

where σ is Stefan-Boltzmann's constant, being 1.356×10^{-12} (cal cm⁻² sec⁻¹ deg⁻⁴) and ε_w the emissivity of the total hemi-spherical radiation of water, being 0.918⁷⁾.

In Fig. 7 the results of calculations for κ_r/κ_a are given. It will readily be seen that for dry air this ratio is represented approximately by a linear function of dry-bulb temperature.

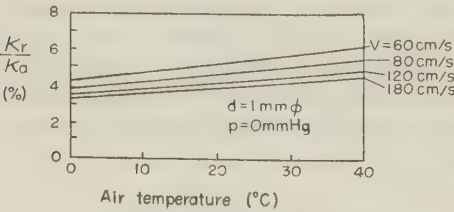


Fig. 7. Relation between radiation correction factor and air temperature for dry air.

In the following, details of the experiments will be described.

(a) *Measurements on dry air in the chamber of constant temperature*

A psychrometer with a wet-bulb moistened with sufficient quantity of water was inserted in the chamber through the upper introducing pipe, and the difference of dry- and wet-bulb temperatures was measured with a potentiometer for a while. Dry-bulb temperature was always observed by another thermocouple and a potentiometer. An example of the results of measurements is shown in Fig. 8. The temperature of water used to moisten the wet-bulb just before insertion into

the chamber was made as equal to the equilibrium temperature as possible, but the indication of the temperature of the wet-bulb immediately after insertion appeared quite different according as it was lower or higher than the equilibrium temperature. Curve I in Fig. 8 corresponds to the case when the temperature of moistening water was lower than the equilibrium temperature, while curve II shows the opposite case. These variations with time seem, in early stages, to be due to the lag of indications of the psychrometer (mainly, of the wet-bulb) and the galvanometer, and, after elapse of some durations, to be due to the rise of humidity by evaporation of water in the interior of the chamber.

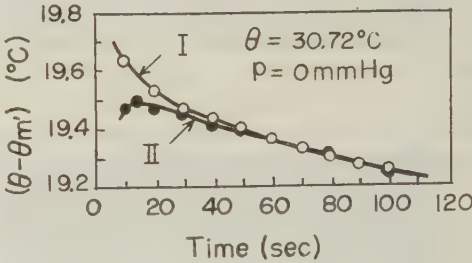


Fig. 8. Change with time of wet-bulb temperature depression after insertion of the psychrometer.

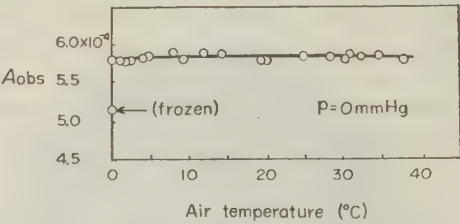


Fig. 9. Experimental results showing A_{obs} versus air temperature, observed in dry air chamber.

By comparison of curves I and II it may be taken that the time lag is about 20 sec and that among other later changes steady deviation due to the lag of the galvanometer indication is trifling. Extrapolation of such curves to the initial time may be assumed to give the correct difference of dry- and wet-bulb temperatures. In effect, judging from a rough calculation of the evaporation velocity, approximately linear extrapolation is considered to give nearly correct values. A more adequate method of circulating dry air was devised, but comparison of the results of the two methods shows that the extrapolation

method gives sufficiently reliable results. Fig. 9 shows the results of measurements. As was expected, the constant A takes a nearly constant value in the whole range of $0^{\circ}\sim 40^{\circ}\text{C}$ of the dry-bulb temperature, the experimental value exceeding the theoretical one by only about 4%.

(b) *Measurements on dry air by the circulation method*

In the present method the wet-bulb temperature remained very nearly constant during some interval from a time a little after insertion of the psychrometer to the time at which the moistened cloth began to dry. Thus, it may be said that there is no fear of increasing humidity and partial drying of moistened cloth. The results of measurements are shown in Fig. 10. It will be seen that the results are nearly equal to those in the former case (a), but slight difference is found in high temperature range, namely, A_{obs} decreases gradually with the increase of temperature, the difference between the two cases being about 1.5% at $\theta=33^{\circ}\text{C}$. Considering the difficulty of extrapolation in the former case (a), owing to rather rapid increase of humidity at high temperature, the results obtained in the present case may be regarded more reliable.

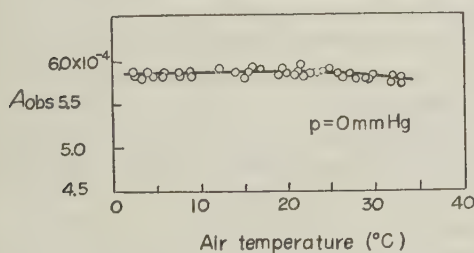


Fig. 10. Experimental results showing A_{obs} versus air temperature, observed in dry air circulating apparatus.

(c) *Measurements on air of various temperatures and humidities in the chamber of constant temperature and humidity*

Relation between humidity and the concentration of sulphuric acid was found, referring to the data compiled by R. E. Wilson⁸⁾. Different relations between these quantities were given by several authors, and though the difference between them is only slight, yet it causes fairly large errors in the measurements connected with the minuteness of the

temperature depression of the wet-bulb. It is, therefore, not easy to get satisfactory quantitative conclusion by these measurements, but nearly expected results were obtained. Following the illustration of theoretical calculation in Fig. 2, Fig. 11 shows the experimental results for A_{obs} at various temperatures and humidities. Curves have been taken by taking the value of A_{obs} , 5.85×10^{-4} , for dry air as standard. It will be seen that though fairly large errors may occur, the observed constant, A_{obs} , for any temperature and humidity decreases at higher temperatures and humidities in accordance with the theory.

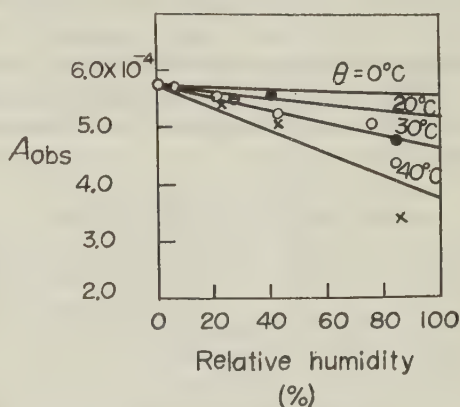


Fig. 11. Experimental results showing A_{obs} at various temperatures and humidities. ($\odot$ at $\theta=20^{\circ}\text{C}$; $\bullet$ at 30°C ; $\times$ at 40°C)

(d) *Effect of pressure*

Experiments were carried out by adjusting the resistance in the circulation path, thus altering the pressure at the position of insertion of the psychrometer. The pressure was only lowered than the atmospheric pressure, but the results may be applied to the alteration of pressure in the region of nearly ordinary atmospheric pressure. As an example, the result in the case of rather large change of pressure will be given, where the atmospheric pressure $P=655$ mmHg (being about 14% lower than the ordinary atmospheric pressure), the water vapor pressure $p=0$ mmHg, the dry-bulb temperature $\theta=22.44^{\circ}\text{C}$, and the wet-bulb temperature $\theta'_m=5.51^{\circ}\text{C}$.

The value of A corrected for radiation was found as:

$$A_{\text{obs}} = 5.85 \times 10^{-4}.$$

Since this value is equal to the measured

value in case of the ordinary atmospheric pressure, it may be concluded that the constant A is independent of pressure.

(e) *Effect of size and shape of wet-bulb*

A psychrometer of different size and shape from those used in the previous experiments was constructed and the psychrometer constant A was examined by the circulation method. As shown in Fig. 12, its dimension was similar to those of psychrometers of mercury-in-glass thermometers. The moistened cloth was covered sufficiently long in order to exclude heat conducted through the stem. An example of the measurements is given below.

In case when the atmospheric pressure $P=749$ mmHg, the water vapor pressure $p=0$ mmHg, the air temperature $\theta=9.97^\circ\text{C}$, and the wet-bulb temperature $\theta'_m=0.37^\circ\text{C}$, the apparent psychrometer constant was obtained as:

$$A_{\text{app}} = \frac{p_{m'}}{P(\theta - \theta'_m)} = 6.80 \times 10^{-4},$$

and the ratio κ_r/κ_a was estimated to be 15~20%.

Thus, the value of the constant A as corrected for radiation becomes

$$A_{\text{obs}} = 5.8 \times 10^{-4},$$

which is in good agreement with the value obtained by small psychrometers. This result may be taken to give a basis for the inference that it is principally due to the effect of radiation that A seems to be different for different psychrometers as well as under different conditions of use, and that the true value of A remains unaltered.

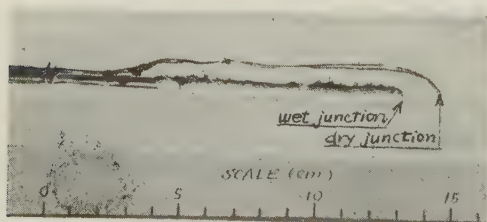


Fig. 12. Psychrometer with different geometry from those No. 1 and No. 2.

(f) *Observations when wet-bulb temperature was below 0°C*

In this case, a wet-bulb may have been supercooled or frozen, giving different values for A . In order to find correct humidity,

therefore, correct judgement should be made whether the wet-bulb is supercooled or frozen. Thus, observations about these points will be described somewhat in detail.

The condition of air within the limits of the experiments was that the humidity was zero and the lowest temperature was 0.05°C . At this lowest temperature the wet-bulb was cooled below -6°C , but the bulb was supercooled in some cases and frozen in the other cases, irrespective of whether there was ventilation or not. Freezing seems to have occurred somewhat more frequently under ventilation, but it cannot be said decisively because of meagre observations. It may be probable that possibility of freezing is fairly large under ventilation. In fact, there were cases in which supercooled water of the wet bulb in still air became frozen by the commencement of ventilation. The judgement whether the wet-bulb was frozen or not was easily made from the change of indication of the wet-bulb temperature after insertion of the psychrometer into the chamber. An illustrative course will be given below.

After insertion, the wet-bulb temperature decreased gradually and fell down below 0°C , approaching an equilibrium state, but, when freezing occurred, it rose suddenly to 0°C . The temperature then remained at 0°C for some time-interval, being about 2.5 min in still air and about 40 sec in a wind of velocity of about 60 cm/sec respectively, and then fell gradually again and finally arrived at the equilibrium state, inspection after drawing-out of the psychrometer having indicated clearly freezing of the bulb. Fig. 13 gives examples of such observations showing the change with time of the difference of dry- and wet-bulb temperatures (galvanometer deflection due to thermoelectromotive force be-

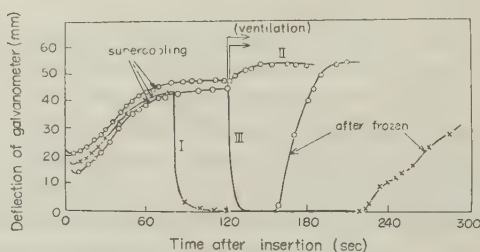


Fig. 13. Change of wet-bulb depression after insertion of the psychrometer in dry air at 0.05°C .

ing nearly proportional to the temperature difference).

In this figure, two arrows in the upper part indicate the commencement of ventilation. Curve I shows the result in case when freezing began without stirring of air. In this case wet-bulb temperature fell down gradually after completion of freezing. Curve II shows the case when the temperature arrived at equilibrium in the state of supercooling and remained supercooled, though wet-bulb temperature fell down by stirring of air. Lastly, curve III shows the result in case when freezing began at the instant of commencement of ventilation.

Owing to the increase of humidity due to evaporation, wet-bulb temperature rose gradually when a psychrometer was inserted into the chamber. When wet-bulb was in the state of supercooling its temperature change followed the same course in repeated experiments, while in the state of freezing it followed various courses and a sweeping statement could not be made. In the case of freezing the speed of temperature rise is larger than in the case of supercooling, sometimes being fairly rapid. These phenomena may be explained by the fact that the thickness of frozen layer is different at different parts and thinner parts are dried more rapidly into which excess heat flows. In the case of supercooling, circulation of water will be facilitated by capillarity so that the whole surface of wet-bulb will be moistened pervasively, thus causing no such phenomena. Some instances of the observations are shown in Fig. 14.

Here, curves I and II show the cases of supercooling, while curves III, IV and V illustrate those of freezing.

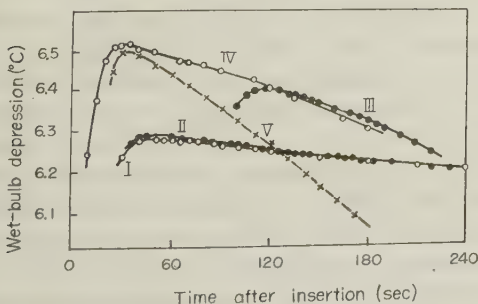


Fig. 14. Change of wet-bulb depression after insertion of the psychrometer in dry air at 0.05°C .

strate those of freezing. In the case of curve III, a wet-bulb moistened with water was inserted into the chamber and was frozen spontaneously. Since, in this case, it took fairly long time before complete freezing, the increase of humidity was somewhat large. Thus, extrapolation to the time of insertion may give inaccurate results. In such a case, therefore, it will be recommended to insert a wet-bulb frozen beforehand with other cooling devices. Curves IV and V were obtained by this procedure. Curve V may probably be considered to be the case when partial drying mentioned before has occurred. Since, however, variation with time of wet-bulb temperature after insertion is nearly the same as those in the cases of curves III and IV, it seems highly probable that there was no partial drying. Thus, wet-bulb temperature corresponding to zero humidity at the time of freezing may be obtained by extrapolation.

When wet-bulb temperature was somewhat high, the air temperature having been about $0.9^{\circ}\sim 8^{\circ}\text{C}$, wet-bulb was always supercooled irrespective of stirring. But, when a wet-bulb was frozen beforehand, it remained still frozen after insertion.

From these experiments it may be inferred that in the case of a wet-bulb with similar size to the present wet-bulb the probability of occurrence of nuclei for freezing is very small when wet-bulb temperature is higher than about $-5^{\circ}\sim -6^{\circ}\text{C}$. It seems that a wet-bulb will become easily frozen if a large water drop is produced on the bulb locally, depending on the quantity of applied water. But this inference has not been confirmed, as the wet-bulb was observed outside on rare occasions by taking out from the test chamber. Again, when repeated experiments were performed at dry-bulb temperature of approximately 0°C , there occurred cases in which a wet-bulb became supercooled repeatedly and also cases in which it became frozen repeatedly. Thus, it seems probable that if freezing has occurred once, nuclei for freezing would be produced easily after then, notwithstanding that distilled water was always used. The phenomena may be considered to depend upon dimensions of psychrometers and conditions of their use. With psychrometers using mercury-in-glass thermometers, wet-bulb are of large dimensions and moisten-

ing water is plenty, hence causing high probability of freezing. So, it is necessary to make sure of freezing when wet-bulb temperature falls down below 0°C .

Lastly, values of the constant A in the cases of supercooling and freezing will be compared in case when dry-bulb temperature $\theta=0.05^{\circ}\text{C}$, wet-bulb temperature $\theta'_m=-6.30^{\circ}\text{C}$ (supercooling) and -6.55°C (freezing), and the atmospheric pressure $P=755\text{ mmHg}$.

We have

$$A_{\text{obs}}=5.85 \times 10^{-4} \text{ (supercooling) ,}$$

$$A_{\text{obs}}=5.11 \times 10^{-4} \text{ (freezing) ,}$$

so that

$$\frac{A_{\text{obs}} \text{ (freezing)}}{A_{\text{obs}} \text{ (supercooling)}}=0.876 .$$

This value is in satisfactorily good agreement with the theoretical value, 0.883, for the ratio of latent heats of vaporization of ice and water.

(g) *Ratio of coefficients of transfers of heat and mass, κ_a/γ*

Experimental values for the ratio κ_a/γ , which has a theoretically important meaning, are shown in Fig. 15 as a function of the algebraic mean of dry- and wet-bulb temperatures. A full-line gives the theoretical curve, and white and black circles give respectively observed values obtained for dry air in the chamber and those obtained for dry air in the circulating apparatus. It will be seen that these two sets of values agree within experimental errors in low temperature range, but there are slight differences in high temperature range, the values denoted by black circles being more reliable. Although the experimental values are greater by about 4% and 2.5% in low and high temperature ranges than the theoretical values, yet the differences may be assumed insignificant by remembering complexity of the phenomena, and agree-

ment between the theory and experiments may be considered to be fairly satisfactory. Further discussion will be added later in this connection. All the observed values were obtained with a wet-bulb of diameter of 1mm for dry air subject to ventilation, but nearly the same values were obtained in cases of a psychrometer with different size, of humidity other than 0%, or of still air, with somewhat larger errors.

(h) *Other results*

Further experiments including measurements in still air and in air subject to various conditions of ventilation were carried out, and comparison was also made with a dew-point hygrometer which detected photoelectrically the change of quantity of reflected light caused by formation of dew on the surface. Only the results will be summarized here.

The conclusion is that, in the case of still air and of air subject to various conditions of ventilation, the correction term for radiation seems to be of right order and the change of wet-bulb temperature with ventilation can be accounted for quantitatively as due to the change of the effect of radiation. Next, it is found that correct determination of humidity by the dew-point hygrometry is very difficult, since the quantity of reflected light decreases gradually in fairly wide range of temperature and the true dew-point cannot be defined without using another standard hygrometry, so that psychrometry performed carefully provides rather more accurate results for ordinary purposes. It seems that the dew-point hygrometry becomes powerful in the case of extremely low humidity.

§ 6. Discussion

As shown in the preceding sections, results obtained in the present experiment are in fairly good agreement with the theory except slight differences in values of the psychrometer constant A . The differences are about 4% in low temperature range, but decrease with the increase of temperature, becoming 2.5% at $\theta=33^{\circ}\text{C}$. These magnitudes may be considered to be small if complexity of the phenomena is taken into account, but are not within experimental errors which are estimated to be less than 1%. The differences may perhaps be attributed, to some extent,

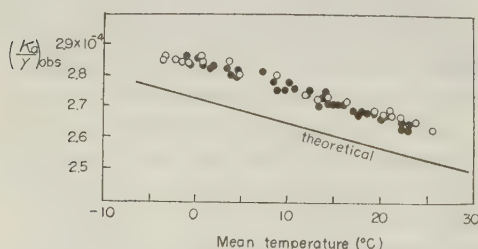


Fig. 15. Experimental results showing relation between the ratio κ_a/γ and mean temperature.

to uncertainty of the values of various physical constants appearing, but mostly to other reasons.

Here we consider about the formula for the transfer of heat adopted previously in which the exponent to Prandtl number has been taken as 0.3. If, however, we assume the exponent to be 0.5, the values of the constant A would become greater by about 3.7% than in the former case, approaching the experimental values in low temperature range, though it would become slightly larger than the observed ones in high temperature range, namely, by about 1.2% at $\theta=33^\circ\text{C}$. The tendency of decreasing of A at high temperatures may be attributed to the effect of thermal diffusion which was not considered previously. Such an effect is negligibly small at low temperatures but increases with the increase of temperature. If we take this circumstance into account, the value of A should decrease theoretically by about 0.8% at $\theta=33^\circ\text{C}$ for dry air and therefore the net differences would become less than 1% throughout the whole temperature range in the present experiment. Thus the experimental values are represented nearly completely by the formula when we take the exponent as 0.5.

The results of the present experiment which has dealt with only air and water vapor system are not sufficient for determining definitely the value of the exponent, but they seem to suggest that it is highly probable to give the value of 0.5 for the exponent instead of 0.3 as usually taken. Another basis of adopting the value of 0.5 is given by L. V. King's theory on the transfer of heat for a circular cylinder immersed in a perfect fluid³⁾, which is represented by the formula:

$$\frac{\kappa_a d}{K} = \frac{1}{\pi} + \left[\frac{2}{\pi} \left(\frac{d\rho v}{\eta} \right) \left(\frac{C_p \eta}{K} \right) \right]^{0.5},$$

and is proved to be in satisfactorily good agreement with experiments.

§7. Summary and Conclusion

The results of the present experiment carried out for determining the psychrometer constant by means thermocouple psychrometers may be summarised as follows.

(1) It is principally due to radiation from surroundings and conduction of heat through the stem that indication of a psychrometer,

and accordingly the so-called 'psychrometer constant' A varies with the size and shape of a wet-bulb and also with ventilation even under fixed temperatures and humidities, and the true psychrometer constant is hardly influenced by such factors.

(2) The constant A is expressed as a function of temperature and humidity, and takes a nearly constant value almost irrespective of temperature for dry air at ordinary temperatures. But it decreases at higher temperatures and humidities owing to the additional term of the conversion calculation.

The theoretical value of A for dry air in the temperature range of $0^\circ\sim 40^\circ\text{C}$ is about 5.6×10^{-4} , while its experimental value is found as $5.8\times 10^{-4}\sim 5.9\times 10^{-4}$, decreasing slightly with the increase of temperature. A slight discrepancy of about 4% or so between these two values may be considered as insignificant owing to the nature of available data and the difficulty of experiments. It is also confirmed that the behavior of A at higher temperatures and humidities is similar to that predicted by the theory.

(3) A takes different values according as a wet-bulb is frozen or supercooled, and the ratio of the corresponding two values seems to be equal to the ratio of the latent heats of vaporisation in the two cases, as again expected from the theory.

(4) It seems that A is not affected by the atmospheric pressure.

(5) The ratio of coefficients of transfers of heat and mass, κ_a/γ , is expressed approximately by a linear function of the algebraic mean of dry- and wet-bulb temperatures. In a certain range of temperatures, it is independent of humidity, ventilation, size and shape of a wet-bulb, condition of freezing or supercooling, but it varies as inversely proportionally to the pressure. Comparison with values for κ_a/γ obtained experimentally shows that fairly good agreement is found between the theoretical and experimental values, the latter being greater by only about 4% or less.

(6) The above comparisons are made on the basis of McAdams' formula for heat transfer, in which the exponent to Prandtl number is taken as 0.3. But, if we assume the exponent to be 0.5 and take the effect of thermal diffusion into account, the agreement between the theoretical and experimental results would

become nearly complete. This suggests that the value of 0.5 should be adopted as the exponent in place of 0.3.

If we use the psychrometer constant thus determined and exclude or minimize various errors, humidity can be measured sufficiently accurately, because a small difference in the values of the psychrometer constant will give rise to only small effect upon the inquired wet-bulb temperature, and the accuracy of psychrometry depends exclusively upon the accuracy of temperature measurement.

Acknowledgements

The writer wishes to express his cordial thanks to Professor S. Kawata for his kind guidance throughout the present work. Thanks

are also due to the Ministry of Education for a grant-in-aid.

References

- 1) S. Kawata and Y. Ômori: J. Phys. Soc. Japan **8** (1953) 768.
- 2) W. Pohlhausen: Z. angew. Math. Mech. **1** (1921) 83.
- 3) L. V. King: Phil. Trans. A, **214** (1914) 373.
- 4) W. H. McAdams: *Heat Transmission* (McGraw-Hill Co., 1942) 222.
- 5) M. Trautz and W. Müller: Ann. Physik **22** (1935) 333.
- 6) M. Trautz and A. Zundel: Z. tech. Phys. **12** (1931) 273.
- 7) E. R. G. Eckert: *Introduction to the Transfer of Heat and Mass* (McGraw-Hill Co., 1950) 277.
- 8) R. E. Wilson: Industr. Engng. Chem. **13** (1921) 326.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 4, APRIL, 1960

The Dynamic Bulk Viscosity of Polystyrene and Polymethyl Methacrylate

By Ryusuke KONO

Department of Applied Physics, Defence Academy, Yokosuka

(Received December 4, 1959)

The transverse and longitudinal wave measurement on polystyrene and polymethyl methacrylate was carried out at frequencies of 0.5, 1, and 2.25 Mc, in the temperature range 20°C to 190°C. For the transverse wave measurement, a modified rotating plate method was used. An energy-dissipating process associated with volume deformation was found in these polymers. The activation energy associated with shear deformation is somewhat different from that associated with volume deformation, so that the molecular mechanism involved in the two types of deformation may be different.

§ 1. Introduction

In recent years an energy-dissipating process associated with volume deformation for high polymers has been studied by several workers.¹⁾ The results obtained on this subject are rather contradictory. One of the experimental difficulty which has been preventing one from reaching conclusion is the shear wave measurement on elastomers in which shear waves are highly attenuated. Since the samples must be mechanically jointed to

transmission block when the solid transmission path is used, in order to generate the transverse wave into the samples, many errors can be introduced at the interfacial joints with the samples. For examples, it is not possible to ensure perfect uniformity in jointing.

For this reason, a modified rotating plate method in which transmission medium is liquid was used for the transverse wave measurement.

It is the purpose of this work to present the results of the transverse and longitudinal wave measurement on polystyrene and polymethyl methacrylate as a function of temperature and frequency.

As usually known, for the propagation of longitudinal and transverse waves in a viscoelastic medium, if steady-state sinusoidal time dependence of stress and strain is achieved, the complex bulk modulus will be written as $K^* = K_1 + iK_2 = K_1 + i\omega\zeta$ and the complex shear modulus $G^* = G_1 + iG_2 = i\omega\eta$, where ζ is the dynamic bulk viscosity, η the dynamic shear viscosity and ω the radian frequency. If the longitudinal-wave modulus is written as $M^* = M_1 + iM_2 = K^* + 4/3G^*$, the relations among the velocity, the attenuation and the modulus at a given radian frequency ω can be shown as follows:

$$G_1 = \frac{\rho v_t^2 \left(1 - \frac{\alpha_t^2 v_t^2}{\omega^2}\right)}{\left(1 + \frac{\alpha_t^2 v_t^2}{\omega^2}\right)^2} \quad (1)$$

$$G_2 = \frac{\rho v_t^2 \frac{2\alpha_t v_t}{\omega}}{\left(1 + \frac{\alpha_t^2 v_t^2}{\omega^2}\right)^2} \quad (2)$$

$$M_1 = K_1 + 4/3G_1 = \frac{\rho v_l^2 \left(1 - \frac{\alpha_l^2 v_l^2}{\omega^2}\right)}{\left(1 + \frac{\alpha_l^2 v_l^2}{\omega^2}\right)^2} \quad (3)$$

$$M_2 = K_2 + 4/3G_2 = \frac{\rho v_l^2 \frac{2\alpha_l v_l}{\omega}}{\left(1 + \frac{\alpha_l^2 v_l^2}{\omega^2}\right)^2} \quad (4)$$

where v_l represents the velocity of longitudinal waves, v_t the velocity of transverse waves, α_l the attenuation of longitudinal waves in nepers/cm, α_t the attenuation of transverse waves in nepers/cm.

Therefore from the measured value of v_l , v_t , α_l and α_t , G_1 , G_2 , K_1 and K_2 can be obtained. The results reported in this paper were obtained from measurements at 0.5 Mc, 1 Mc and 2.55 Mc and in the temperature range 20°C to 190°C.

§ 2. Experimental method

The schematic diagram of the apparatus for the longitudinal and transverse wave measurement is shown in Fig. 1. The synchroscope triggers the pulse generator of radio

frequency at a constant time interval. The oscillations are fed to the transmitting crystal, which generates the pulsed ultrasonic wave traveling into the liquid. This wave is picked up by the receiving crystal and the resultant signal is amplified and fed into the synchroscope. When a sample is in the path of the beam, the wave pattern on the synchroscope screen changes in amplitude and

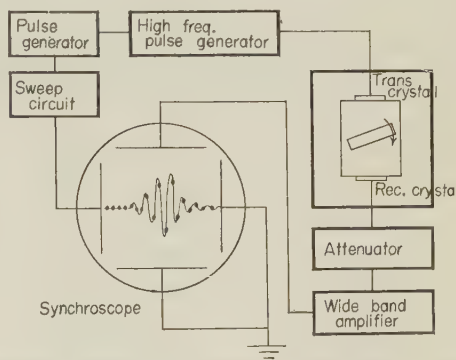


Fig. 1. Schematic diagram of apparatus for measuring longitudinal and transverse wave propagation constants.

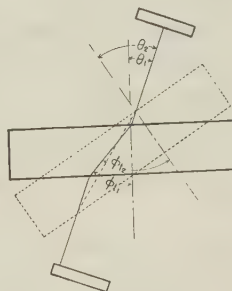


Fig. 2. Measurement of transverse wave velocities.

the attenuation of longitudinal wave in the sample can be obtained. When the sample thickness is changed by rotation, interference patterns result due to reflections at the interfaces. From the measurement of total reflection angle θ_l , the velocity of longitudinal wave can be obtained from the relationship $v_l = c/\sin \theta_l$,²⁾ where c is the velocity in the liquid. In this work silicone oil was used as transmission medium and the velocity in it was measured by pulse method.

The velocity of transverse wave can be obtained by the modified rotating plate method. That is, the sample is put at such an angle that the longitudinal waves are totally reflected. Then the sample is rotated from θ_l

to Θ_2 , as shown in Fig. 2, the wave pattern on the synchroscope screen shifts in position, if there is a difference between the velocity in the liquid and that in the samples. When

the time shift Δt is measured by time marker of synchroscope, the velocity of transverse wave in the sample is obtained from the relations:

$$v_t = \frac{d(\cos \varphi_2 - \cos \varphi_1)}{\Delta t \cos \varphi_1 \cos \varphi_2 + (d/c)\{\cos \varphi_2 \cos(\varphi_1 - \Theta_1) - \cos \varphi_1 \cos(\varphi_2 - \Theta_2)\}} \quad (5)$$

$$\frac{c}{v_t} = \frac{\sin \Theta_1}{\sin \varphi_1} = \frac{\sin \Theta_2}{\sin \varphi_2} \quad (6)$$

Table I. Influence of thickness upon transverse wave velocities for a series of polymethyl methacrylate sheets.

	<i>d</i> cm	<i>d</i> /λ	<i>v</i> m/s		<i>d</i> cm	<i>d</i> /λ	<i>v</i> m/s		<i>d</i> cm	<i>d</i> /λ	<i>v</i> m/s
0.5 Mc	1.997	7.4	1337	1 Mc	0.981	7.3	1337	2.25 Mc	0.413	6.9	1358
"	1.051	3.9	1331	"	0.500	3.7	1327	"	0.201	3.3	1347
"	0.695	2.6	1335	"	0.375	2.8	1300	"	0.104	1.7	1306
"	0.491	1.8	1288	"	0.117	0.9	1286	"			
"	0.287	1.0	1269	"				"			

where Θ_1 and Θ_2 represent the incident angle, φ_1 and φ_2 the angle of refraction, d sample thickness and Δt the time shift observed by rotation of the sample from Θ_1 to Θ_2 . At first the value of v_t is appropriately assumed. Then v_t is calculated from the relations (5) and (6) by a successive approximation.

Measured values for the transverse wave velocity in polystyrene and polymethyl methacrylate were checked with those reported in the previous work³⁾ to better than 0.5 percent.

Relations (6) are derived for an infinitely thick sample and are not strictly valid for thin material. In Table I the observed transverse wave velocities are tabulated for a series of polymethyl methacrylate samples of decreasing thickness. It will be noted that variations in the velocities as a result of sample thickness disappear for thickness of 3λ (λ =wavelength), or greater.

The measurement of transverse wave velocity were accurate to within 0.5 percent in thick sample and to 10 percent in thin sample.

When the transverse wave is so highly attenuated at higher temperature, the velocity of longitudinal wave v_l can not be obtained from total reflecting angle Θ_t . The value of v_t was measured by the modified rotating plate method. In this case, when the sample is rotated from Θ_1 ($=0$) to Θ_2 the relations (5) and (6) become to be more simple expres-

sion.

The sample is put at such an angle Θ_1 that the longitudinal waves are totally reflected. Then the sample thickness is changed from d' to d'' . The absorption of transverse wave L_t is obtained from the relations:

$$L_t = \frac{A_t' - A_t''}{d' - d''} \cos \varphi_t \quad (7)$$

$$\sin \varphi_t = \frac{v_t}{c} \sin \Theta_t \quad (8)$$

where A_t' db/cm represents the ratio of the sound transmitted with the sample in the path to the sound transmitted with the sample removed, d' sample thickness.

Measured value for L_t satisfactorily coincides with the one measured by the pulse method.

Polystyrene was moulded from pellets and polymethyl methacrylate prepared by Mitsubishi Rayon Company. All samples used were annealed in the silicone oil and cut from one large block in order to reduce variations between samples. These samples were 0.05 to 4 cm in thickness. The rate of heating was kept almost constant 15 deg/hr.

§ 3. Results

The temperature dependence of longitudinal and transverse wave velocities in polystyrene and polymethyl methacrylate are shown in Fig. 3. At high temperature plastic flow takes

place in polystyrene. So the dashed portions of the curves indicate regions where the data were unsatisfactory. An increase in velocities with increasing frequency is noted even in the glassy region, showing much more dispersion in the transition region.

The curves of longitudinal wave absorption versus temperature in polystyrene and polymethyl methacrylate exhibit peaks in this temperature region as shown in Fig. 4 and 5.

The transverse wave absorption in polystyrene and polymethyl methacrylate are shown in Fig. 6 and 7.

temperature.

The transition temperature of polystyrene is about 85°C and that of polymethyl methacrylate 89°C by the measurement of linear thermal expansion as reported by the previous work.³⁾

As shown in Fig. 8, break points between the real part of the bulk and shear modulus versus temperature curve in polystyrene are observed at about the transition temperature 85°C. As shown in Fig. 5 and 7, the absorptions of longitudinal and transverse waves in polystyrene begin to increase near the transi-

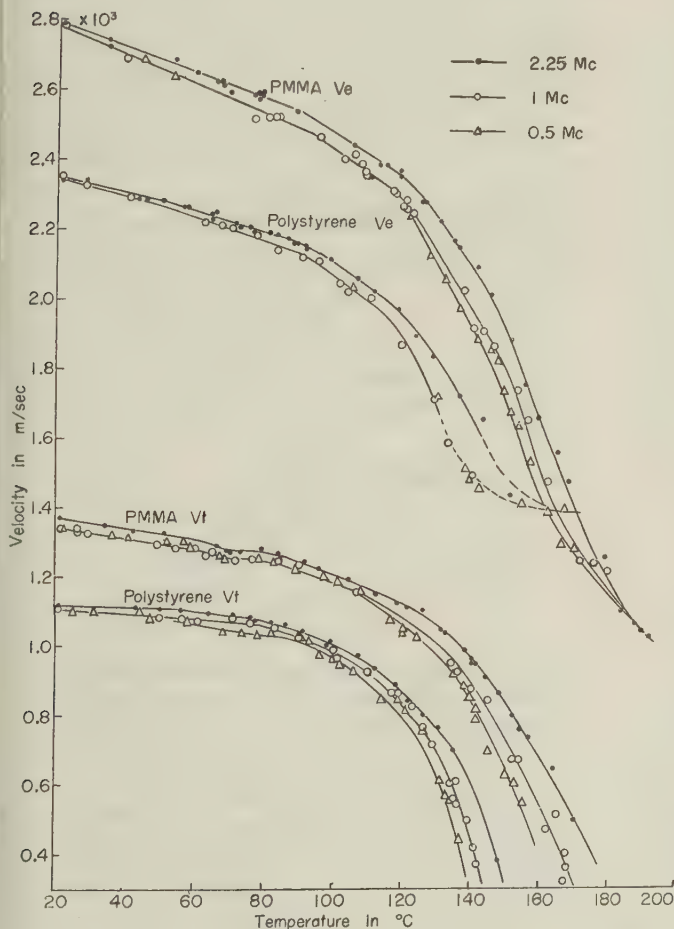


Fig. 3. Longitudinal and transverse wave velocity versus temperature for polystyrene and polymethyl methacrylate.

§ 4. The Real Part of the Modulus

In Fig. 8, the real part of the shear and bulk modulus of polystyrene as well as polymethyl methacrylate, calculated from the smoothed experimental results according to the relation (1) and (3), are plotted against

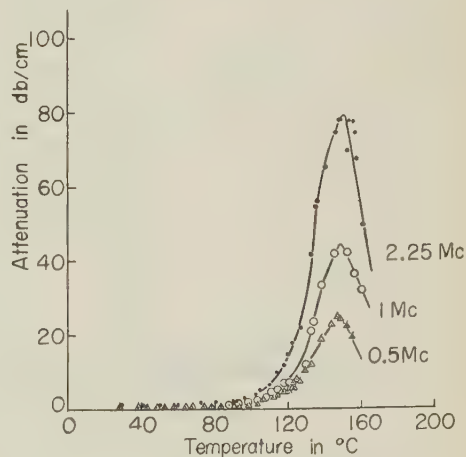


Fig. 4. Attenuation of longitudinal waves per cm for polystyrene at all frequencies.

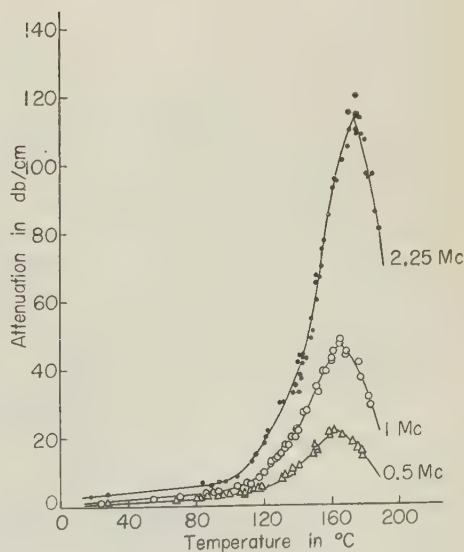


Fig. 5. Attenuation of longitudinal waves per cm for polymethyl methacrylate at all frequency.

tion temperature.

We understand that the relaxation of the shear modulus as well as the bulk modulus occurs near the transition temperature in polystyrene.

As shown in Fig. 8, the break point of the

real part of the shear modulus in polymethyl methacrylate is observed and the absorption of the transverse waves begin to increase near the transition temperature. Therefore the relaxation of the shear modulus occur the transition temperature 89°C in polymethyl methacrylate. The break point of the real part of the bulk modulus have been hardly observed near the transition temperature but at about 120°C. Though the imaginary part of the modulus begins to increase at about 89°C, the relaxation of the bulk modulus markedly occurs near 120°C in polymethyl

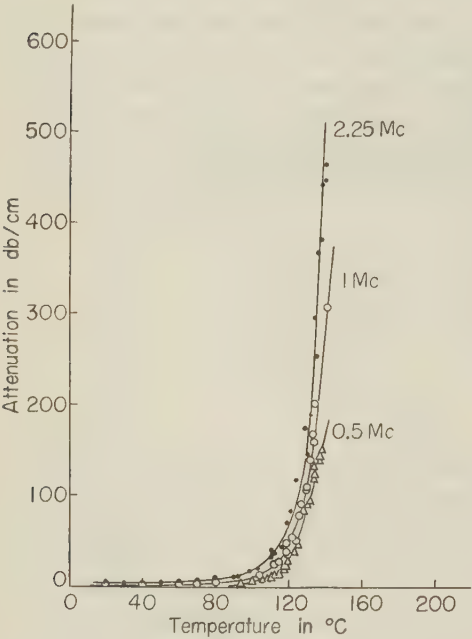


Fig. 6. Attenuation of transverse waves per cm for polystyrene at all frequency.

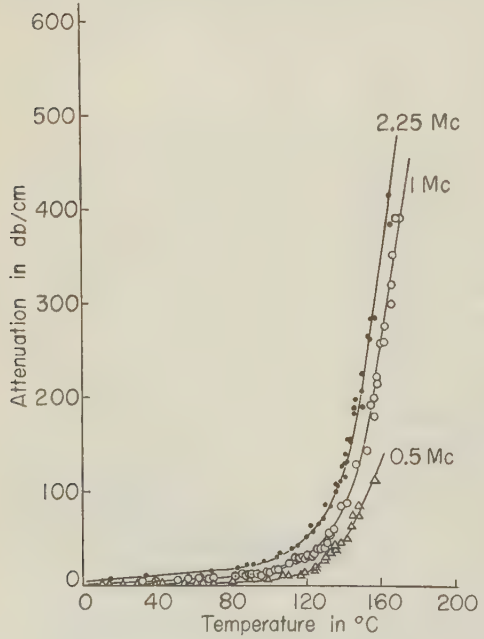


Fig. 7. Attenuation of transverse wave per cm for polymethyl methacrylate at all frequency.

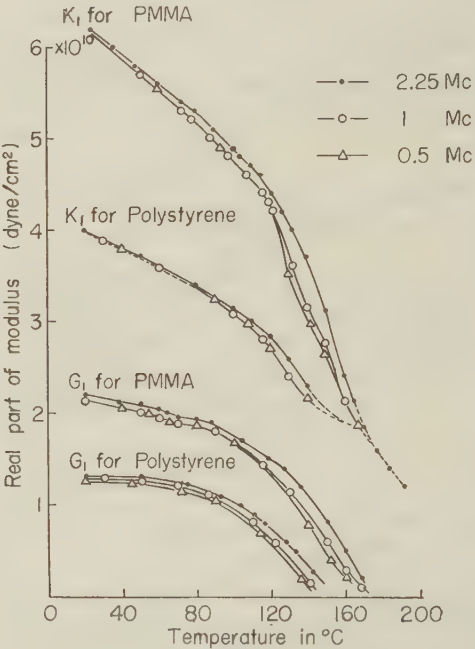


Fig. 8. Real part of the shear and bulk modulus versus temperature for polystyrene and polymethyl methacrylate.

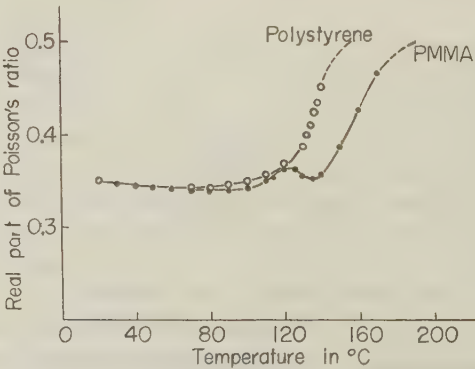


Fig. 9. Real part of the Poisson's ratio versus temperature for polystyrene and polymethyl methacrylate at 1 Mc.

methacrylate.

This difference between the temperature dependences of the both modulus affects considerably the variation with temperature of the Poisson's ratio. The real part of Poisson's ratio σ is given by

$$\sigma = \frac{3K_1 - 2G_1}{6K_1 + 2G_1}.$$

The ratio in polystyrene and polymethyl methacrylate at frequency of 1 Mc are plotted against temperature as shown in Fig. 9.

The ratio in polystyrene is a monotonically increasing function of temperature in the transition region. The ratio in polymethyl methacrylate increases with increasing temperature in the transition region at first and decreases towards a minimum. Then the ratio increases towards the maximum value of 0.5.

§ 5. The Imaginary Part of the Modulus

In Fig. 10 and 11, the imaginary part of

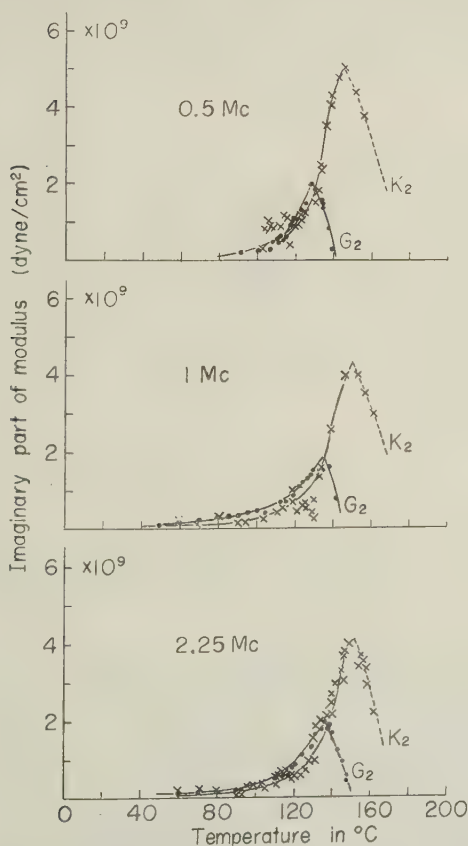


Fig. 10. Imaginary part of the shear and bulk modulus versus temperature for polystyrene.

the shear and bulk modulus of polystyrene and polymethyl methacrylate, calculated from the relation (2) and (4), are shown plotted against temperature.

An accuracy in attenuation measurement is not great enough to permit precise conclusion as to the relations between the shear and volume deformation mechanisms, but it does permit some statements about orders of magnitude.

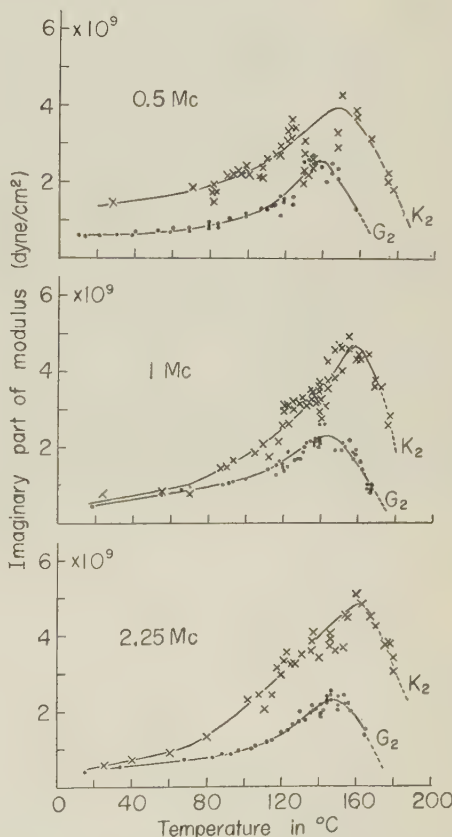


Fig. 11. Imaginary part of the shear and bulk modulus versus temperature for polymethyl methacrylate.

It was not possible to make any measurements for the shear wave in the region shown by the dashed line because the shear wave was highly attenuated in samples. Since the longitudinal waves were measured throughout the temperature range covered, and since the imaginary part of the shear modulus is very small in comparison with that of the longitudinal wave modulus at sufficiently high temperature, the imaginary part of the bulk modulus may be shown by the dotted portion.

For polystyrene and polymethyl methacrylate the imaginary part of the shear modulus G_2 is somewhat smaller than that of the bulk modulus K_2 . A considerable portion of the energy losses of the longitudinal wave in these polymers is due to a bulk viscosity.

There can be no doubt that the temperature at the peak in K_2 is different from that in G_2 .

From reciprocal temperature at the peak versus frequency the activation energies can be obtained. For polystyrene, the activation energies Q_k associated with volume deformation is about 106 Kcal/mol and that Q_G associated with shear deformation is about 62 Kcal/mol.

The value of Q_G for polymethyl methacrylate is obtained about 58 Kcal/mol. But the value of Q_K cannot be obtained, because the temperature at the peak in K_2 is somewhere in the range of 130°C to 160°C at frequency of 0.5 Mc. This may be an error attributable to taking differences between nearly equal quantities.

An extended frequency plot based on the reduced variable technique of Ferry and others⁴⁾ (after making a small correction to the modulus by multiplying the data at tem-

perature T by a factor T_0/T) are shown in Fig. 12. The shifted curves of G_1 , K_1 , G_2 , and K_2 for polystyrene at a reference temperature of 125°C are shown in Fig. 12.

The shifting factor a_T and the activation energy versus temperature of G_1 for polystyrene are shown in Fig. 13. When the log a_T factors for bulk modulus are plotted against $1/T$, a straight line is obtained in the region 120°C to 145°C. The slope of this line is about 80 Kcal/mol. Though it is apparent that activation energy associated with both deformations rise steeply with decreasing temperature as the glass transition temperature is approached, it requires further investigation to obtain the value of activation energy.

These values of activation energies are almost the same to the value obtained from reciprocal temperature at the peak versus frequency. For polystyrene the activation energies associated with shear deformation obtained in this work are comparable to the value measured by Ferry at low frequencies.⁵⁾

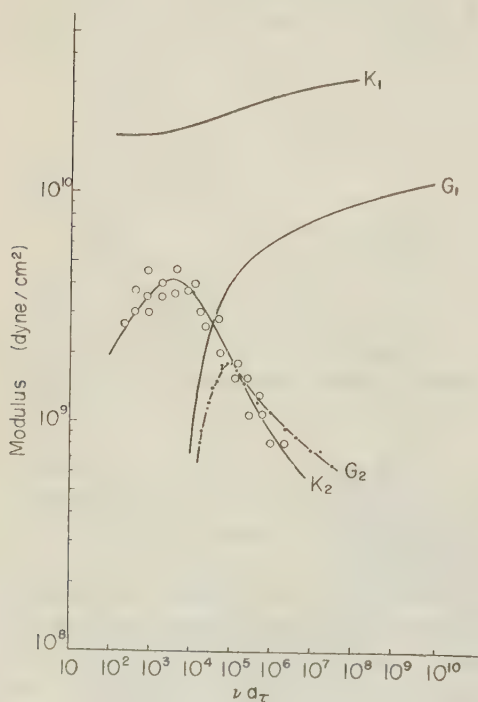


Fig. 12. Real and Imaginary part of the reduced shear and bulk modulus for polystyrene reduced to 125°C.

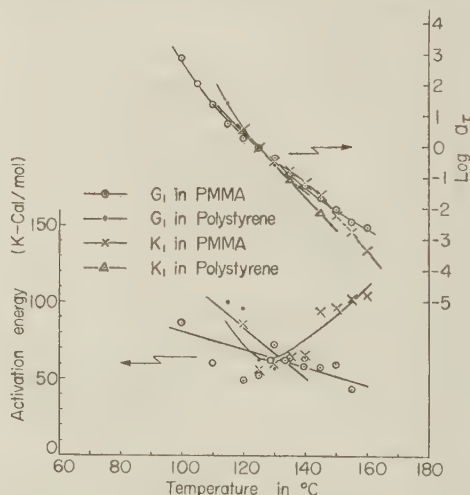


Fig. 13. Shifting factor a_T and activation energy versus temperature for polystyrene and polymethyl methacrylate.

If the reduced variable technique of Ferry is applied to polymethyl methacrylate, frequency shift a_T versus temperature curve of K_1 is irregular as shown in Fig. 13.

As shown in Fig. 8 the real part of the modulus for polymethyl methacrylate in the glassy region as well as in the transition region are more temperature dependent than that of polystyrene.

As shown in Fig. 10 and 11 the imaginary part of the modulus for polymethyl methacrylate is much larger than that for polystyrene in the glassy region. These may imply that the molecular movements of side chains like the ester linkage contribute to the deformation mechanism even in the glassy region. As previously mentioned, the shifting factor a_T versus temperature curve for K_1 in polymethyl methacrylate shows an irregular form. This may also be understood from the molecular movements of side chains. Further conclusion for polymethyl methacrylate will probably have to await an experiment at wider frequencies.

For polystyrene, as shown in Fig. 12, G_1 increases more steeply with increasing frequency than K_1 . The peak in K_2 is somewhere in the range of $\log \nu = 3$ to 4 and that in G_2 occurs at about 4.8. As already mentioned above activation energy for G_2 is somewhat smaller than that for K_2 at the temperature of 120°C to 140°C.

The final conclusions to be drawn from these measurements are that an energy-dissipating process associated with volume deformation is found in these polymers. The

activation energies associated with shear deformation is different from that associated with volume deformation and the former is somewhat smaller than the latter at the temperature of 120°C to 140°C, so that the molecular mechanism in the two types of deformation may be different.

The author wishes to express his sincere thanks to Prof. Y. Ikeda and Prof. T. Soeya for their encouragements and discussions.

References

- 1) A. W. Nolle and P. W. Sieck: J. Appl. Phys. **23** (1952) 888. R. S. Marvin, R. Aldrich and H. S. Sack: J. Appl. Phys. **25** (1954) 1213. J. R. Cunningham and D. G. Ivey: J. Appl. Phys. **27** (1956) 967.
- 2) W. C. Schneider and C. J. Burton: J. Appl. Phys. **20** (1949) 48. Y. Wada: J. Appl. Phys. Japan **24** (1955) 159.
- 3) R. Kono: Kobunshi-Kagaku **14** (1957) 500. (in Japanese) R. Kono: Kobunshi-Kagaku **16** (1959) 203. (in Japanese)
- 4) See, for example, J. D. Ferry: J. Amer. Chem. Soc. **72** (1950) 3746.
- 5) L. D. Grandine and J. D. Ferry: J. Appl. Phys. **24** (1953) 679.

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm×7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 726

Measurement of Piezoelectric Constants of a CdS Crystal

By Toshio TANAKA and Shoji TANAKA

Department of Applied Physics, University of Tokyo, Tokyo

(Received January 16, 1960)

The crystal structure of wurtzite type CdS belongs to space group C_{6v}^4 which should show piezoelectric effects. H. Gobrecht and A. Bartschat¹⁾ have found that CdS crystal actually show piezoelectric effects. The value of piezoelectric constants, however, has not been reported yet.

Let the fundamental piezoelectric equations be

$$\begin{aligned} P &= e \cdot S, & (\text{direct effect}) & (1) \\ P &= d \cdot T, & (2) \end{aligned}$$

and

$$\begin{aligned} T &= e \cdot E, & (\text{converse effect}) & (3) \\ S &= d \cdot E, & (4) \end{aligned}$$

where P is the polarization vector, s is the strain vector, T is the stress vector, E is the electric field and e and d are the piezoelectric stress and strain coefficient tensors respectively. In wurtzite lattice, e and d have three independent components and can be expressed as

$$e = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}$$

and

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}. \quad (5)$$

We measured d_{31} and d_{33} using the relative method adopted by E. Fukada²⁾³⁾. The sample is clamped together with an x-cut quartz plate and a rochelle salt pick up. First, an alternating voltage is applied to the electrodes on the quartz, which produces the piezoelectric strain. The strain is transformed to an electric signal by means of the rochelle salt pick up. The amplitude of the electrical signal is then read on a cathode ray oscilloscope. Next, the amplitude of the electrical signal from the rochelle salt pick up is read, the alternating voltage being applied to the sample. Since the ratio of the amplitudes is equal to that of the strains of two materials, we obtain the strain of CdS sample using the value $d_{11} = 6.9 \times 10^{-8}$ c.g.s. of quartz. The results are shown in Fig. 1.

With the help of Eq. (4), we find from Fig. 1. that

$$|d_{33}| = 7.7 \times 10^{-8} \text{ c.g.s.}$$

and

$$|d_{31}| = 4.6 \times 10^{-8} \text{ c.g.s.}$$

Unfortunately, we could not determine the value of d_{15} because of the shape of the sample. However, it is possible to estimate it from the theoretical relation⁴⁾

$$e_{15} \div e_{31}$$

and so

$$d_{15} = (d_{31}C_{11} + d_{33}C_{31})/C_{44}.$$

The sign of the d 's was not determined from the experiment. However, it is quite natural to assume that d_{33} has a different sign from d_{31} .

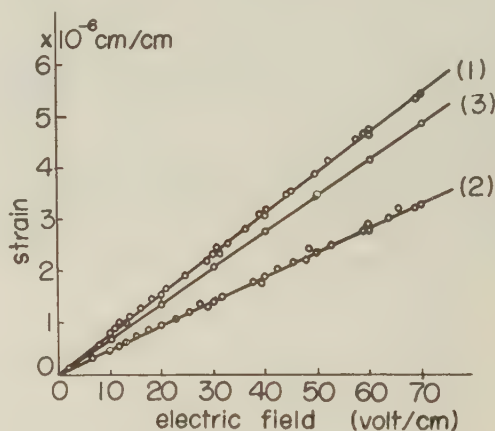


Fig. 1. (1) The strain parallel to the c-axis (S_3) when an electric field was applied parallel to the c-axis. (2) The strain perpendicular to the c-axis (S_1) when an electric field was applied parallel to the c-axis. (3) The strain of x-cut quartz.

The authors wish to express their hearty thanks to Prof., Y. Suge for his encouragements and to Dr. E. Fukada of Kobayashi Institute of Physical Research for supplying the rochelle salt pick up and to Dr. T. Masumi of Institute of Physical and Chemical Research for supplying the CdS crystal.

References

- 1) H. Gobrecht and A. Bartschat: *Z. Physik* **136** (1953) 224.
- 2) E. Fukad: *J. Appl. Phys. Japan* **24** (1955) 299.
- 3) E. Fukada and I. Yasuda: *J. Phys. Soc. Japan* **12** (1957) 1158.
- 4) T. Tanaka and S. Tanaka: to be published.

J. PHYS. SOC. JAPAN 15 (1960) 727

Electrical Conductivity of α -Fe₂O₃*

By Tanehiro NAKAU

*Department of Physics, Faculty of Science,
Kyoto University, Kyoto*

(Received January 27, 1960)

A measurement of electrical conductivity has been performed on natural single crystal samples of α -Fe₂O₃ containing impurities such as Ca, Mg and Sn. Data on polycrystalline samples of pure α -Fe₂O₃ and α -Fe₂O₃ containing Ti were reported and discussed by Morin^{1,2)}. Our experiment was carried out to examine any anisotropy and any anomaly of conductivity expected to be caused respectively by the trigonal symmetry and by the change of the electronic spin arrangement at the transition temperature^{3,4,5,6)}. The experiment showed a certain anisotropy in both the value of conductivity and the slope of the curve of logarithm of conductivity *versus* reciprocal temperature and also an anomaly near the transition temperature.

The sample No. 1 consisted of α -Fe₂O₃ containing 5.4 atomic percent Mg and 2.4 atomic percent Ca and the sample No. 2 of α -Fe₂O₃ containing 3.3 atomic percent Mg and 1.0 atomic percent Sn. They were shaped in rectangular parallelepipeds and their magnetic transition temperature was privately informed by N. Kawai to be -20°C .

The measurement was carried out in the [0001] and [10 $\bar{1}0$] directions referred to the hexagonal axes by the two-contact method using Ag vapor deposited electrodes. The field strength was below 0.4 V/cm in the [10 $\bar{1}0$] direction of each sample, below 1.2 V/cm in the [0001] direction of No. 1 and below 1,600 V/cm in that of No. 2, with the applied voltage not exceeding 80 volts. The results are shown in Figs. 1 and 2, from which the following characters can be recognized.

(1) The slopes of the curves of logarithm of conductivity *versus* reciprocal temperature are quite different for the two different crystallographical directions in No. 2, whereas they are almost equal in No. 1. In both cases, the slope of the curve does not seem to change below and above the transition temperature.

(2) In the [10 $\bar{1}0$] direction of each sample, the curve steps up at the transition temperature with temperature increase, but on the contrary, the curve in the [0001] direction steps down at this temperature, although the curve in the [0001] direction of No. 2 has been roughly plotted below the transition temperature.

It should be noted that each specimen has low

* Read in part before the annual meeting of the Physical Society of Japan, Oct. 11, 1959.

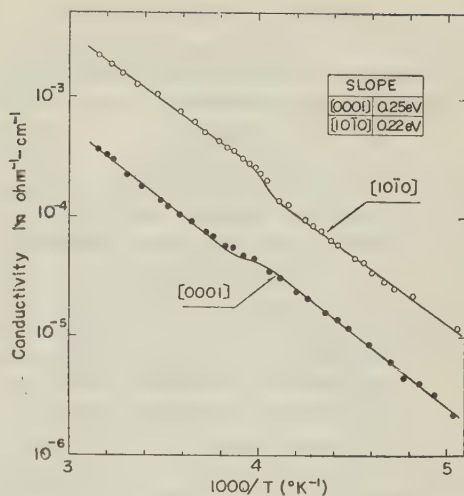


Fig. 1. Conductivity *versus* $1/T$ of the sample No. 1.

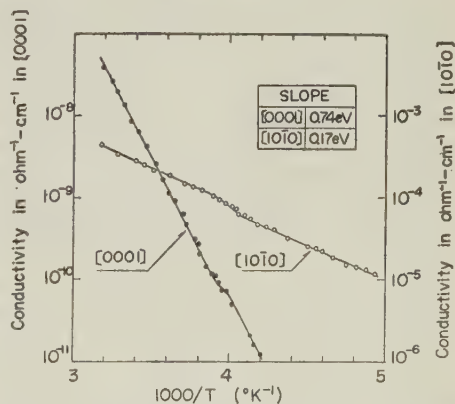


Fig. 2. Conductivity *versus* $1/T$ of the sample No. 2.

conductivity in spite of the presence of much impurity. The fact that neither the step up nor the step down was observed in the data of Morin¹⁾ may probably be due to the circumstance that his samples are polycrystalline.

The author wishes to express his sincere thanks to Professor I. Takahashi for his interest and guidance throughout this work. His thanks are also due to Professor T. Matsubara for valuable discussions and to Dr. N. Kawai for his help in preparing the samples and to Mr. C. Okazaki of Matsushita Elec. Ind. Co. for his chemical analysis.

References

- 1) F. J. Morin: Phys. Rev. **83** (1951) 1005.
- 2) F. J. Morin: Phys. Rev. **93** (1954) 1195.
- 3) K. Néel: Ann. physique **4** (1949) 249.
- 4) E. J. Morin: Phys. Rev. **78** (1950) 819.
- 5) C. G. Shull, W. A. Strauser and E. O. Wollan: Phys. Rev. **83** (1951) 333.
- 6) L. Néel: Rev. Mod. Phys. **25** (1953) 58.

J. PHYS. SOC. JAPAN **15** (1960) 728~729

On the Proton Chemical Shift in Deuterium Substituted *p*-Xylene and Toluene

By Hazime KUSUMOTO

The Institute of Scientific and Industrial
Research, Osaka University, Sakai

Junkichi ITOH

Department of Physics, Osaka University, Osaka

Kozo HIROTA and Tomiko UEDA

Department of Chemistry, Osaka
University, Osaka

(Received January 28, 1960)

Deuterium substitution for some of the protons forming a perfect pairing was found¹⁾ an useful method in the field of high resolution n. m. r. work to investigate the indirect spin-spin coupling²⁾ between these protons. J_{HD} observed in such substituted compounds enables us to estimate $J_{HH'}$ immediately in consideration that the coupling constants are proportional to the products of the magnetogyric ratios of proton and deuteron and a factor depending only on the electronic structure, which is practically unaffected by the deuteration. However, it was noticed recently^{3), 4)}, besides this "isotope effect", that the protons in the CH_2D group of α -deuterotoluene are 0.015 ppm more shielded than those in the CH_3 group of deuterium-free toluene. We also found a similar phenomenon on deuterium substituted *p*-xylene as mentioned elsewhere⁴⁾.

One of the two prepared samples, (I), seemed to contain deuterium-free *p*-xylene, α -deuterated *p*-xylene, $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{D}$, and α, α' -dideuterated one, $\text{CH}_2\text{DC}_6\text{H}_4\text{CH}_2\text{D}$. The other sample, (II), was a statistical mixture of α, α' -dideuterated *p*-xylene, $\text{CHD}_2\text{C}_6\text{H}_4\text{CH}_3-i\text{D}_i$, where $i=0, 1, 2, 3$, and the above mentioned *p*-xylene deuterated. The proton high resolution spectrum was observed with a Varian

4300 B high resolution 40 Mc/sec spectrometer. Typical traces of the "methyl" groups of samples are shown in Fig. 1.

An asymmetrical triplet, the central peak of which is more intense than the outer peaks, was observed obviously in (I). A 1:1:1 triplet equally spaced is expected for the CH_2D group, corresponding to the three spin states of the deuteron ($I=1$). Therefore, the spectrum obtained suggests that the singlet of the CH_3 group is superposed on it and the true triplet is shifted slightly to higher field from the singlet of the CH_3 group. This fact is clearer in a result about CH_2D group of α -deuterated toluene, (III), containing 29% of deuterium-free toluene. Its spectrum could be decomposed into a singlet and a triplet as shown in Fig. 1. Rough estimation of the chemical shift of the protons in the CH_2D was about 0.6 cps to higher field from the protons in the CH_3 group. This result is in good agreement with Tiers' data³⁾.

An asymmetrical quintet was observed in (II). The intensity ratio and spacing of each component deviate considerably from the expected proton spectrum, equal spacing and intensity ratio of 1:2:3:2:1, for the proton in the CHD_2 group. This fact indicates that the spectrum consists of a singlet, a triplet, and a quintet slightly shifting each other. It is noteworthy that the fifth small peak to higher field is clearly resolved but the first one at lower field is almost superimposed on the second one. The third peak has the strongest intensity. If there would be no chemical shift between the CH_2D protons and the CHD_2 one, the two outer component may be resolved identically, because J_{HD} was found about 2.4 cps and the shift was only 0.6 cps on the CH_2D protons of α -deuterated toluene. However, if the CHD_2 proton would be further shifted by the same value, (~ 0.6 cps), to higher field from the CH_2D protons, this asymmetrical line shape could be reproduced with appropriate weighting.

The valence bond theory⁵⁾ and the angular dependence of isotope effect⁶⁾ do not interpret such shifts. Our results, however, suggest that CHD_2 proton is more shielded than the CH_2D protons. Unfortunately the results at present did not give us an exact value of chemical shift between the CH_2D protons and the CHD_2 proton. Further studies on α -mono- and -dideuterated toluene are now in progress.

Reference

- 1) H. S. Gutowsky, L. H. Meyer and R. E. McClue: Rev. Sci. Instr. **24** (1953) 644.
- 2) H. S. Gutowsky, R. E. McClue and C. P. Slichter: J. Chem. Phys. **21** (1953) 279.
- 3) G. V. D. Tiers: J. Chem. Phys. **29** (1958) 963.
- 4) K. Hirota, H. Kusumoto and T. Ueda: (to be published in Bull. Chem. Soc. Japan). Asym-

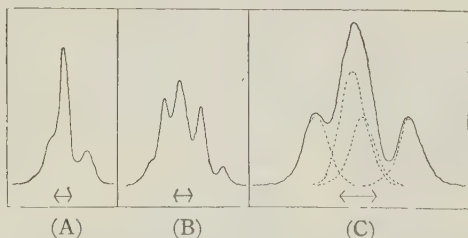


Fig. 1. The proton high resolution magnetic resonance spectra at 40 Mc/sec of the "methyl" groups of (A) deuterated *p*-xylene (I), (B) deuterated *p*-xylene (II), and (C) α -deuterated toluene, respectively. Each arrow indicates 2 cps. The magnetic field increases from left to right.

- metrical singlet and quintet have been reported independently of reference (6).
- 5) M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky: *J. Chem. Phys.* **27** (1957) 597.
M. Karplus and D. H. Anderson: *J. Chem. Phys.* **30** (1959) 6.
- 6) H. S. Gutowsky, M. Karplus and D. M. Grant: *J. Chem. Phys.* **31** (1959) 1278.

J. PHYS. SOC. JAPAN **15** (1960) 729

Cold-emitting Cathode Materials

By Yoshihiko MIZUSHIMA, Yoshitaka IGARASHI
and Tetsuji IMAI

*Electrical Communication Laboratory, Nippon
Telegraph and Telephone Public Corporation
Musashino-shi, Tokyo, Japan*

(Received February 16, 1960)

Since the discovery of cold cathode using $MgO^{(1)}$ we have tested $MgO^{(2)}$ and various other materials for the possibility of cold emission. The oxides were tested in powdered form or smoke if availa-

ble, or by thermal decomposition of suitable compounds. Purities were of commercially high grade. If there existed various forms of the same oxide, tests were carried out on the forms stable in a vacuum.

It was found out that, when they showed a tendency to a field-dependent secondary emission, then after suitable treatment they became mostly cold-emitting. This property were found to depend strongly on the preparation of cathode.

The result for powdered metal oxides on platinum substrates are shown in Table I. As is seen there, useful oxides belong to the II, III and IV-famililies. The oxides concerned have high specific resistivity and high secondary emission factor (δ), so far as are known. The powders have relatively high melting points, stable in vacuum at high temperature and their appearance are all white. These facts indicate that the oxide itself must be a good insulator, having a wide energy-band gap. It does not seem likely that there exist any other common physical properties, for instance such as crystallographic structures. Corresponding luminescent colours very widely.

Some sulfides and carbides (CdS, SiC etc) were

Table I. Metals corresponding to tested oxides are written in heavy letter, of which cold-emitting materials are indicated with bold line. Light line means field-dependent secondary emission, but very rarely cold-emitting at room temperature.

I	II	III	IV	V	VI	VII	VIII
H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
	Cu Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru Rh Pd
	Ag Cd	In	Sn	Sb	Te	I	
Cs	Ba	La*	Hf	Ta	W	Re	Os Ir Pt
	Au Hg	Tl	Pb	Bi	Po	At	
Fr	Ra	Ac	Th				

* but not Ce.

also tested, with no success. It was also found that some luminescent materials, such as silicates and tungstates ($CdWO_4$, $ZnSiO_3$ etc) proved to be cold-emitting, with their characteristic luminescence.

The most powerful material so far is MgO , with maximum current density of about 100 mA/cm^{-2} and with luminous efficiency of maximum 20%.

References

- 1) A. M. Skellet, C. G. Firth and D. W. Mayer: *Proc. Inst. Radio Engrs.* **47** (1959) 1704.
2) T. Imai, Y. Mizushima and Y. Igarashi: *J. Phys. Soc. Japan* **14** (1959) 979.

J. PHYS. SOC. JAPAN **15** (1960) 730

Tunneling Probability in Germanium $p-n$ Junctions

By Yoshitaka FURUKAWA

The Electrical Communication Laboratory,
Musashinoshi, Tokyo

(Received February 29, 1960)

L. Esaki¹⁾ showed that the tunneling current in narrow $p-n$ junctions is given by

$$Z \int \{f_c(E) - f_v(E)\} \rho_c(E) \rho_v(E) dE$$

where Z is the tunneling probability, $\rho_c(E)$ is the state density of the conduction band, $\rho_v(E)$ is the state density of the valence band.

As the maximum tunneling currents, $I_{\max}$, appear at nearly constant forward bias voltages, the variation of $I_{\max}/\text{cm}^2$ with carrier concentration in germanium is controlled predominantly by the change in Z .

For step junctions, Z ²⁾ is given by

$$\exp\left\{-\frac{\pi^2 m^{*1/2} k^{1/2} E_g}{eh} (1/n + 1/p)^{1/2}\right\},$$

though, as Keldysh³⁾ pointed out, this is only an approximate formula. Therefore, it may be expected that $\log I_{\max}/\text{cm}^2$ versus $(1/n + 1/p)^{1/2}$ curve shows a straight line with slope

$$-\frac{\pi^2 m^{*1/2} k^{1/2} E_g}{eh}.$$

To examine this relation, Esaki diodes have been made by alloying indium balls (0.5% Ga + 99.5% In) onto the As- or Sb-doped germanium. The alloying has been carried out under the same condition throughout this work.

Fig. 1 shows resistivity versus carrier concentration curves. The carrier concentration, n , has been determined by using the relation $R=1/en$ and the factor⁴⁾ arising from the band structure has not been taken into account in this calculations.

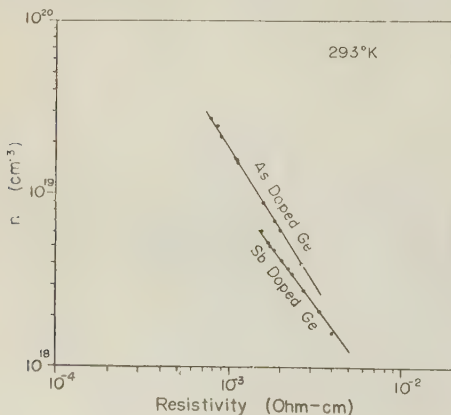


Fig. 1.

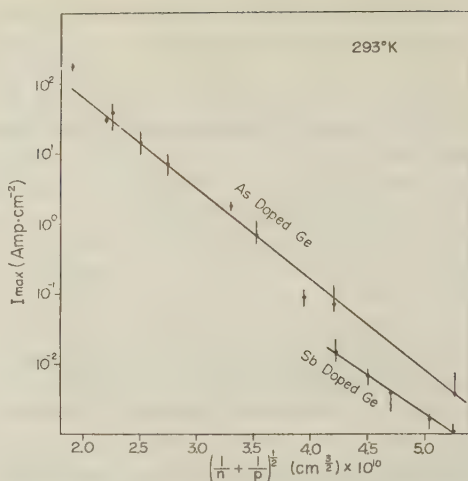


Fig. 2.

For the same electron densities, the mobilities in Sb doped germanium are larger than those in As doped germanium. Spectroscopic analysis shows that these differences are not due to the compensation effects.

Fig. 2 shows $\log I_{\max}/\text{cm}^2$ versus $(1/n + 1/p)^{1/2}$ curves. The hole concentration in the p -side of the junctions has not been determined directly but assumed to be 10^{20} cm^{-3} . As expected above, straight lines have been obtained and its slope is -2.72×10^{10} for Sb-doped germanium and -3.16×10^{10} for As-doped germanium. These values are nearly equal to the theoretical one. From the simple theory, the slope is given by -3.2×10^{10} using $m^*=0.08m$.

As will be seen from Fig. 2, $I_{\max}/\text{cm}^2$ depends on the specific donor impurities. It cannot be expected from the simple hydrogen-like model that the electrical properties of germanium vary with the impurities. These phenomena may be explained qualitatively by the change of the state density or the change of the effective mass with the specific impurities, and related to the fact⁵⁾ that only the diode made of Sb-doped germanium exhibits wiggle in its current-voltage curve at 4°K .

The author thanks Dr. T. Niimi heartily for the encouragement in the course of this work. He is also indebted to Messrs Y. Kanai, T. Takahashi and T. Shimozaki for their interest in the present investigation.

References

- 1) L. Esaki: Phys. Rev. **109** (1958) 603.
- 2) McAfee et. al.: Phys. Rev. **83** (1951) 650.
- 3) L. V. Keldysh: Soviet Physics JETP **6** (1958) 763.
- 4) C. Herring: B. S. T. J. **34** (1955) 237.
- 5) N. Holonyak, I. A. Lesk, R. N. Hall, J. J. Tiemann and H. Ehrenreich: Phys. Rev. Letters **3** (1959) 167.

J. PHYS. SOC. JAPAN **15** (1960) 731**180° Domain Wall Motions in BaTiO₃ Crystal**

By Kazuo HUSIMI

*Electrical Communication Laboratory
Musashino City, Tokyo*

(Received February 16, 1960)

180° domain wall motion in BaTiO₃ crystal under a low field has been observed by R. C. Miller¹⁾, and this arouses us an interest on the domain wall motion of BaTiO₃ crystal in high field switching.

Fig. 1 shows a photograph of the domain growth obtained by repeating KCl etching four times after application of a low field for about one minute each time. The velocity of domain wall motion is large along [100] direction as reported by R. C. Miller.



Fig. 1. Domain growths under a low field.

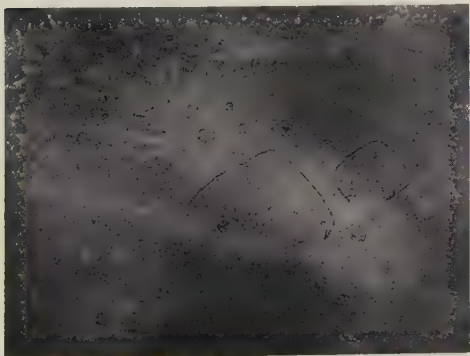


Fig. 3. Domain growths under a high field.

is applied after the domain growth by the pulse field of the same field strength but opposite polarity for four times. Many shrinked domains are nearly circular.

From these experiments, we conclude that in the case of high field application up to about 5 kv/cm, the polarization reversal is also performed by side-wise domain wall motion as in the case of low field switching, though many nucleuses of new antiparallel domain appear.

In Fig. 2 is shown domain shrinks obtained by etching two times, the first after a domain growth by application of a negative low field for about one minute, and the second after a shrinkage of the growth domain by application of the field with same strength but positive polarity for about five seconds. Domain shrinkage begins from the corners of the square, so the domain patterns become octangle, and then square with sharp 90° edges. Their diagonal direction are along [110] axes.

Fig. 3 shows a high field domain growth obtained by application of negative 5 kv/cm, 0.3 μsec pulse field for four times on the crystal which has previously grown a low field etch figure. Differing from the low field case, it is shown in this figure that the square domains have sharp 90° edges and their diagonal axes lie along [110] direction.

The domain shrinkage at high field is also shown in Fig. 4. In this case, the high single pulse field

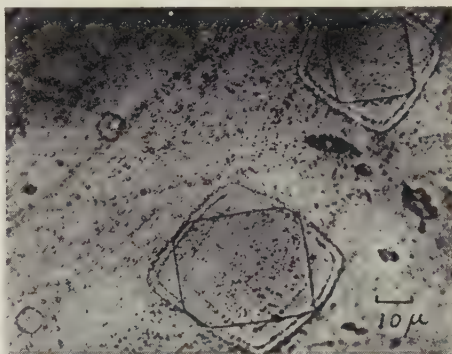


Fig. 2. Domain shrinks under a low field.

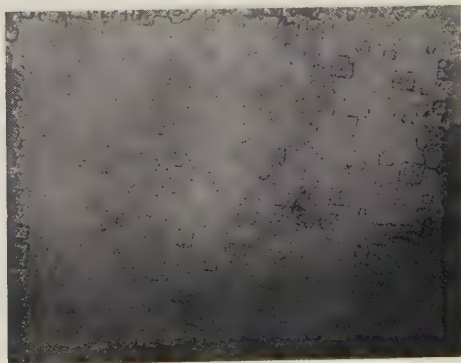


Fig. 4. Domain shrinks under a high field.

Change of diagonal axes of the etch patterns from [100] to [110] by increase of applied field has also been observed by R. C. Miller²⁾.

Theoretical treatment of these observations is also in progress by T. Nakamura³⁾ on the kinematic wave theory.

References

- 1) R. C. Miller: Phys. Rev. **111** (1958) 736.
- 2) R. C. Miller: Phys. Rev. **115** (1959) 1176.
- 3) T. Nakamura: to be published.

J. PHYS. SOC. JAPAN **15** (1960) 732

The Dislocation Etch Pits of CdS Crystals

By Jiro NISHIMURA

*Faculty of Art and Literature, Iwate University
Morioka, Japan*

(Received February 9, 1960)

The distribution of the etch pits on the (0001) plane of a CdS single crystal reveals interesting tendencies differing with the growing conditions of the crystal, when etched with thiourea-HCl solution at 60°C for 5 min^{1),2)}. Photo. (1) shows the (0001) etch figure of the crystal prepared by sublimation and recrystallization at 930°C for 48 hours in H₂S. The subgrain boundaries run along $\langle 10\bar{1}0 \rangle$ direction in almost whole region of the etched surface except near the intersections of the subboundaries. For brevity we designate them as type (1) boundaries. Photo. (2) shows that of the crystals prepared at 1050°C for 72 hours in H₂S. In this case there appear, instead of type (1) boundaries, the arrays of pits running along $\langle 12\bar{1}0 \rangle$ directions, which we designate as type (2) boundaries. When the crystals grow at 950°~1000°C for 72 hours, both types of boundaries are observed, which is shown in

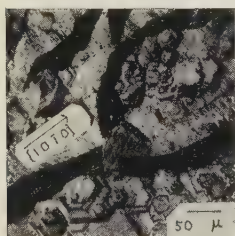


Photo. 1.

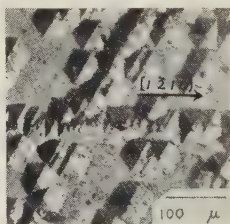


Photo. 2.



Photo. 3.



Photo. 4.

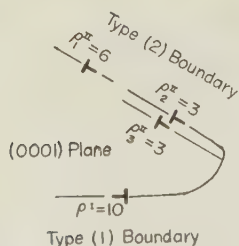


Fig. 1.

Photo. (3). With the etch figure presented in Photo (4), these boundaries are confirmed to be the arrays of edge dislocations: If ρ^I and ρ^{II} denote the number of pits per unit length of type (1) and the *i*th of type (2) boundaries respectively, as depicted in Fig. (1), the following relations hold among these ρ 's.

$$\rho^I = 1.7\rho^{II} \simeq \sqrt{3}\rho^{II}, \quad (1)$$

$$\rho^{II} = \rho_2^{II} + \rho_3^{II}. \quad (2)$$

These equations agree with what the theory of the low-angle symmetric boundary predicts, if we assume that type (1) and type (2) boundaries are the arrays of the edge dislocations with Burgers vector $\mathbf{a}\langle 12\bar{1}0 \rangle$ and slip plane $\{10\bar{1}0\}$, and with Burgers vector $\sqrt{3}\mathbf{a}\langle 10\bar{1}0 \rangle$ and slip plane $\{12\bar{1}0\}$ respectively. (Here $\mathbf{a}$ denotes the magnitude of the lattice vector to the direction $[12\bar{1}0]$ and, therefore, $\sqrt{3}\mathbf{a}$ is equal to the magnitude of lattice vector to $[10\bar{1}0]$).

Hence we are led to the following conclusions: The subgrain boundaries which run along $\langle 10\bar{1}0 \rangle$ direction on $\{0001\}$ surfaces are sets of parallel edge dislocations with Burgers vector $\mathbf{a}\langle 12\bar{1}0 \rangle$ and slip plane $\{10\bar{1}0\}$. This type of dislocation walls are formed in more or less stressed crystals. Another type of dislocation walls is formed in the crystal which is heated at high temperature for prolonged duration. The walls of this type are the ones with Burgers vector $\sqrt{3}\mathbf{a}\langle 10\bar{1}0 \rangle$ and slip plane $\{12\bar{1}0\}$. It is presumed that the imperfections which have aligned themselves to be edge dislocations of type (1) alter their arrangement to form the dislocation walls of type (2) after the prolonged heat-treatment in H₂S. It is believed that the dislocation walls play an important role in the activation of the crystals³⁾. Details will be presented later.

The author wishes to acknowledge with thanks the instructive discussions with Prof. M. Yamamoto of Research Institute for Iron, Steel and other Metals, Tohoku University. He also wishes to express thanks to Prof. T. Hibi and Prof. Y. Tanabe of Research Institute of Scientific Measurements, Tohoku University, for kind encouragement and to Mr. H. Fujisaki and Mr. T. Matsumura of Tohoku University for the helpful discussions.

References

- 1) R. F. Brebrick and W. W. Scanlon: J. Chem. Phys. **27** (1957) 607.
- 2) J. Nishimura: J. Appl. Phys. Japan **29** (1960) to be published.
- 3) S. Ibuki and H. Yamashita: J. Phys. Soc. Japan **14** (1959) 1827.

J. PHYS. SOC. JAPAN 15 (1960) 733~734

Piezoresistivity in Semiconductive Barium Titanates

By Osamu SABURI

Technical Laboratory, Murata Manufacturing Co., Ltd. Nagaoka-cho, Kyoto, Japan.

(Received January 6, 1960)

Remarkable temperature dependency of the piezoresistivity was observed in the system of semiconductive (Ba,Sr)TiO₃ doped with cerium, which has an anomalous positive temperature characteristic of the resistivity¹⁾.

Specimens were prepared in the form of a bar, whose dimensions were 2 mm, 2 mm and 10-16 mm in width, thickness and in length respectively, having different compositions in the (Ba,Sr)TiO₃ system and doped with 0.1 mole % of Ce. A set of In-Hg electrode of 2 mm square was put either on the end surfaces, or at the centers of the two opposite rectangular sides. The resistivity change was measured by a resistance bridge between the electrodes, while a mechanical pressure was applied.

The resistivity changes at the pressure of 360 kgr/cm² are shown in Fig. 1 and 2, as the longitudinal and transversal piezoresistivity, respectively.

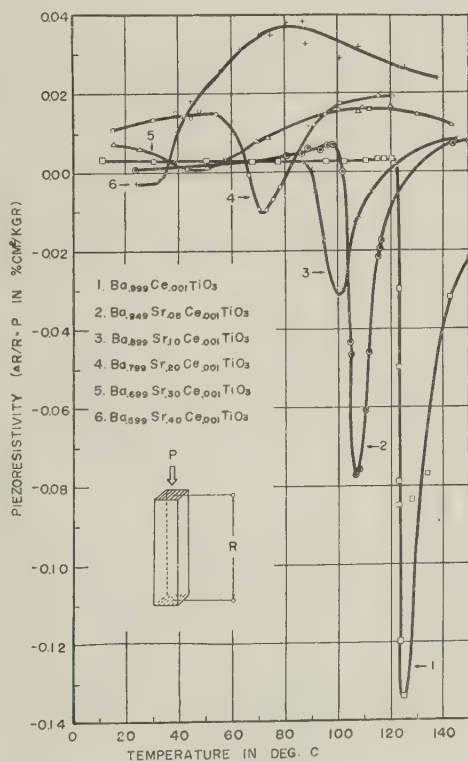


Fig. 1. Temperature dependency of longitudinal piezoresistivity of different materials in the (Ba,Sr)TiO₃ system.

(Actually, at the temperature far below or above the Curie point, the resistivity changes linearly with the pressure, while in the neighborhood of the Curie point it follows the relation: $\Delta R/R = ap^b$ (where $1 < b < 2$)).

The piezoresistivity, whichever longitudinal or transversal, is small at the temperature far below the Curie point, and shows the negative peak in the neighborhood of the Curie point, which depends upon the Sr content. Above the Curie point, the piezoresistivity decreases rapidly, changes sign and tends to a positive value asymptotically. The negative peak of the piezoresistivity which occurs at the Curie point becomes higher with decreasing content of Sr, and reaches $-0.135\%/kgr/cm^2$ ($1.38 \times 10^{-9} cm^2/dyne$) in BaTiO₃.

For each composition of the body, the temperature-piezoresistivity curve is very similar to the curve of temperature vs. temperature coefficient of resistivity. For the transversal piezoresistivity, the ratio of the piezoresistivity at the Curie point and at 360 kgr/cm² vs. the temperature coefficient of the resistivity at the said point, remains almost constant, that is,

$$\Delta R/R \cdot P \cong k \cdot \Delta R/R \cdot \Delta t \quad \text{or} \quad \Delta t = k \cdot P,$$

where the constant k is equal to about $-1.3 \times 10^{-3} ^\circ C/kgr/cm^2$. For the pressure of 360 kgr/cm², the above relation gives the temperature decreasing of 0.47°C. According to the study of H. Jaffe et al.²⁾ for the BaTiO₃ ceramics, the effect of pressure

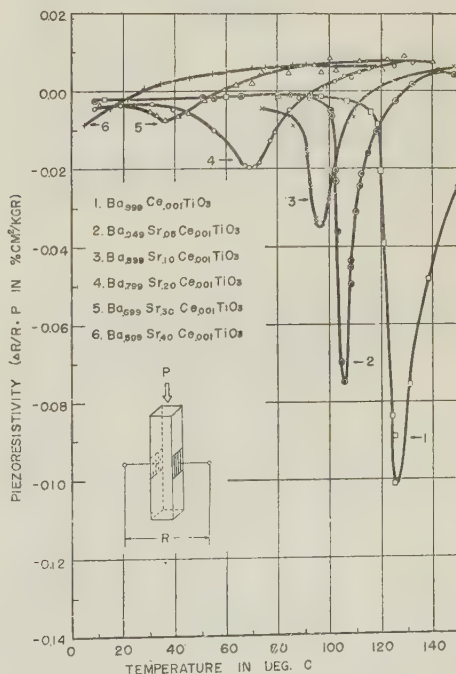


Fig. 2. Temperature dependency of transversal piezoresistivity of different materials in the (Ba,Sr)TiO₃ system.

upon the shift of the Curie point is expressed by the equation:

$$T_c = T_0 + 3.31 \times 10^{-6} P^2 \quad (T \text{ in } ^\circ\text{C}, P \text{ in kgr/cm}^2).$$

Provided P is 360 kgr/cm² in the above equation, the rising of the Curie point is 0.43°C, which is approximately equal to the value of temperature decreasing obtained above.

The above behaviors would lead us to suppose that, when the pressure is applied, the resistivity decreases at the Curie point with the following mechanism. The steep positive temperature characteristic of the resistivity occurs in relation to the Curie point, and the rising of the Curie point caused by the pressure effects upon the resistivity-temperature characteristic of the resistivity, causing the shift of resistivity-temperature curve towards higher temperature.

The piezoresistivity in semiconductive barium titanates observed by Sauer et al.³⁾ with the hydrostatic pressure at room temperature might be regarded as corresponding to the values at room temperature of our results, and the considerable difference between the values of Sauer et al. and ours may be supposed to be caused by the difference of the method of applying mechanical pressure; hydrostatic in Sauers study, uniaxial in ours.

The writer wishes to express his sincere gratitude to Dr. K. Abe, Professor Emeritus of Kyoto University and Dr. T. Tanaka, Professor of Kyoto University, for their valuable guidance.

References

- 1) Osamu Saburi: J. Phys. Soc. Japan **14** (1959) 1159.
- 2) Hans Jaffe, Don Berlincourt and J. M. McKee: Phys. Rev. **105** (1957) 57.
- 3) H. A. Sauer, S. S. Flaschen and D. C. Hoes-terey: J. Amer. Cer. Soc. **42** (1959) 363.

J. PHYS. SOC. JAPAN **15** (1960) 734~735

Magnetic Susceptibility of CoBr₂·6H₂O*

By M. GARBER

Physics Dept., Michigan State University,
E. Lansing, Michigan

(Received February 4, 1960)

Forstat and Spence¹⁾ recently reported N.M.R. and specific heat data showing an antiferromagnetic transition in CoCr₂·6H₂O at $T_N = 3.08^\circ\text{K}$. This note gives some recent results of static susceptibility measurements in the liquid helium region.

* Supported by Office of Ordnance Research, U. S. Army.

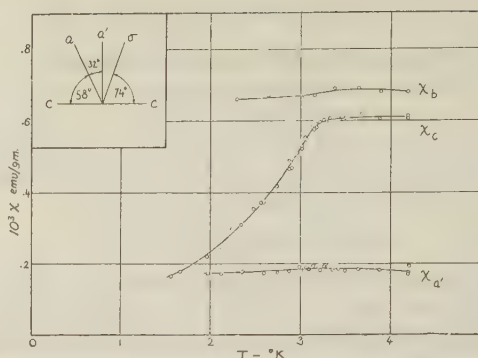


Fig. 1. Magnetic susceptibility of CoBr₂·6H₂O below 4.2°K. Inset shows the various crystallographic and magnetic axes in a plane normal to the b -axis.

These were made on single crystals by the Faraday method, using a Sucksmith balance calibrated against iron ammonium sulphate. The monoclinic crystals of CoBr₂·6H₂O are isomorphous with those of CoCl₂·6H₂O and are described in Groth²⁾. Fig. 1 inset shows the disposition of the c , a and σ axes in a plane perpendicular to the b -axis. Specimens with well developed faces were selected and oriented by means of light reflection from freshly cleaved c -planes.

The results are shown for the external field oriented along the three principal axes. Two of these coincide with the crystal b and c axes and the third, a' , is mutually perpendicular to these two and lies about 32° from the a -axis. The c -axis is the preferred spin alignment direction as it is also in some other cases (CoCl₂·6H₂O³⁾, MnCl₂·4H₂O⁴⁾, MnBr₂·4H₂O⁴⁾). It was determined by plotting susceptibility vs. angle in the a - c plane at various temperatures above and below the Néel point.

The knee in the χ -parallel curve occurs at about 3.2°K , or slightly higher than the transition temperature observed by N.M.R. and specific heats. This general feature has been noted a number of times previously⁴⁾. The measurements were made at 1500 oe., so that the above temperature corresponds nearly to the zero field case. No critical field was observed up to 5000 oe.

The susceptibilities at 80°K were determined also, the values being $\chi_a = 0.026 \times 10^{-3}/\text{gm}$, $\chi_b = 0.123 \times 10^{-3}/\text{gm}$, $\chi_c = 0.118 \times 10^{-3}/\text{gm}$. The flat region which extends above the Néel temperature agrees with the large specific heat tail (38% of ΔS occurs above 3.2°K)¹⁾.

The author wishes to thank Dr. R. D. Spence and Dr. J. M. Daniels (U.B.C.) for their advice.

References

- 1) H. Forstat, G. Taylor and R. D. Spence: Phys. Rev. (Nov. 15, 1959).

- 2) P. Groth: *Chem. Krist.* **1** (1908) 248.
- 3) T. Sugawara: *J. Phys. Soc. Japan* **14** (1959) 1248. R. B. Flippen and S. A. Friedberg: in press (1960).
- 4) H. M. Gijssman: Thesis, Leiden (1958).

J. PHYS. SOC. JAPAN **15** (1960) 735

Some Experiments on Plasma Alfvén Waves

By Shigeo NAGAO and Teruyuki SATO

*Engineering Faculty, Tohoku
University*

(Received February 16, 1960)

We have attempted, independently of Allen et al.¹⁾, to generate transverse hydromagnetic waves (Alfvén waves) in a plasma in a linear glass tube, and to measure the phase velocity and attenuation of the waves in ionized air at rather weak magnetic fields. The present note reports some results of the preliminary experiments with a future view to resonating such a wave in magnetic mirrors. The discharge tube used is 60 cm long with a 30 cm diameter. At each end of this cylindrical tube, there is a ring electrode 12.5 cm in diameter with a 1.5 cm bore and a coaxial ball electrode 3 cm in diameter. One couple of these ball-ring electrodes is used to generate waves and another couple to detect them transmitted along the magnetic field in a plasma. The tube is pre-ionized by the discharge of a condenser bank (475 V, $7 \times 10^4 \mu\text{F}$) between these two couples at both ends. This current flows in the central cylindrical region of the tube with a diameter a little larger than that of the ring electrode and reaches a maximum value of 10 kA in 600 μsec , when the magnetic field produced by the other condenser discharge also becomes maximum. Then, in order to generate Alfvén waves the third condenser (10 kV, 0.5 μF) is discharged between a ball and a ring electrode at one end. This current oscillates a few times at the frequency 170 K.C. with a maximum value of 3 kA.

When waves arrived at the other end, the radial drop of electric potential between a ball and a ring electrode which are short-circuited outside the discharge tube was measured by a Rogowsky coil and displayed on an oscilloscope. Traces of the oscilloscope triggered by the current generating the waves give time lags and amplitudes of the transmitted waves. Dependencies of the velocity and amplitude upon the magnetic field B_z , gas pressure p and pre-ionization current I_{pi} are given in Fig. 1. Though the wave frequency is not so small compared to the ion cyclotron frequency,

these dependencies show rather good agreements with theory, especially at large magnetic fields and small gas pressures. The attenuation of waves were estimated approximately by the ratio of the potential between a ball and a ring electrode at both ends. The magnetic field and pressure dependency of the wave attenuation seems to be reasonable.

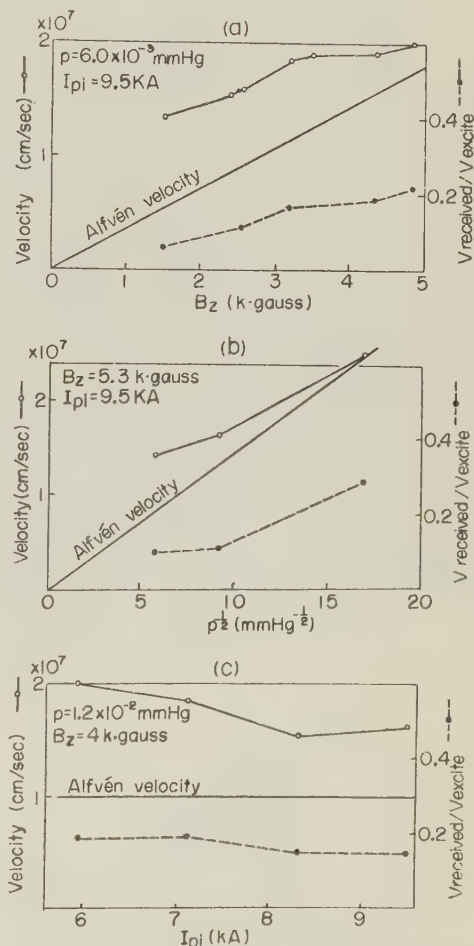


Fig. 1. Dependencies of velocity and amplitude upon B_z (axial magnetic field), p (gas pressure) and I_{pi} (pre-ionization current).

Because of the imperfect ionization and finite conductivity of the gas, the wave nature was affected to some extent by the magnitude of the pre-ionization currents.

It was also remarked that the frequency of waves differs several per cent at both ends.

Reference

- 1) T. K. Allen et al.: *Phy. Rev. Letters* **2** (1959) 383.

J. PHYS. SOC. JAPAN **15** (1960) 736~737**A Gamma Ray in Ti^{45} Decay**

By Chikai ISHII and Kasuke TAKAHASHI†

*Department of Physics, Tohoku University
Sendai*

(Received January 6, 1960)

No gamma ray has been reported so far in the decay of Ti^{45} . On the other hand Sc^{45} has been known to have rather many lowlying excited states whose energy values have been found from the inelastic scattering of protons¹⁾. Among these states, there can be some states to which some positron branchings of order of a percent or so may occur since the decaying energy is enough. Such a branching will be detected by the observation of gamma rays in Ti^{45} . If one finds such a gamma ray, it will give a further information on the properties of $(f_{7/2})^n$ configurations, on which considerable interest has been taken lately.

Very pure (five nine) metallic titanium was activated by the 25-Mev bremsstrahlung from a betatron in the internal target²⁾ for producing the Ti^{45} activity ($T_{1/2}=3.1$ hr) from the reaction $Ti^{46}(\gamma, n)Ti^{45}$. In order to investigate the gamma rays from Ti^{45} , the gamma rays in coincidence with one of the 0.51-Mev gamma rays created by the positron annihilations were looked for using a fast-slow

coincidence circuit ($2T=80$ m μ sec). Two NaI(Tl) crystals of the same size ($1\frac{1}{2}'' \times 1\frac{1}{2}''$) were used at the right angle each other. The irradiated titanium sample was placed at about 4 cm from the face of each crystal. Such a geometry was selected so that the photopeaks of the positron pair may not be counted in coincidence. This was essential for detecting gamma rays below ~ 0.5 Mev in the presence of strong positrons. Here, the use of very small samples bombarded in the internal target was advantageous since the scattered annihilation radiation coming into one crystal in coincidence with the 0.51-Mev peak in another crystal could be minimized. The gamma ray pulses from the detector were connected to a 100 channel pulse height analyser through the gate of the fast-slow coincidence circuit. The 1.277-Mev gamma ray following the positron decay of Na^{22} was used for the intensity calibration.

In addition to known gamma rays from nuclides produced from photoreaction on titanium isotopes with this energy a weak gamma ray of 0.38 Mev decaying with a half life of ~ 3 hr was found (Fig. 1). This gamma ray is assigned to the transition from the first excited state of Sc^{45} at 0.377 Mev. The intensity of this gamma ray was found to be approximately 0.3 percent of the total decay. This is considered to be due to a positron plus K-capture branching to the 0.377-Mev state and the $\log ft$ value for the transition between the ground state of Ti^{45} and the 0.377-Mev state of Sc^{45} is then calculated to be 6.2

A very weak gamma ray of 0.541 Mev may exist, but its relative intensity was less than 0.1 percent. Accordingly, the $\log ft$ value is estimated to be 6.5 or larger.

It is well established that the ground state of Sc^{45} has $7/2^-$. On the other hand the first excited state at 0.377 Mev has only been reported by Windham et al.¹⁾ and nothing more has been known.

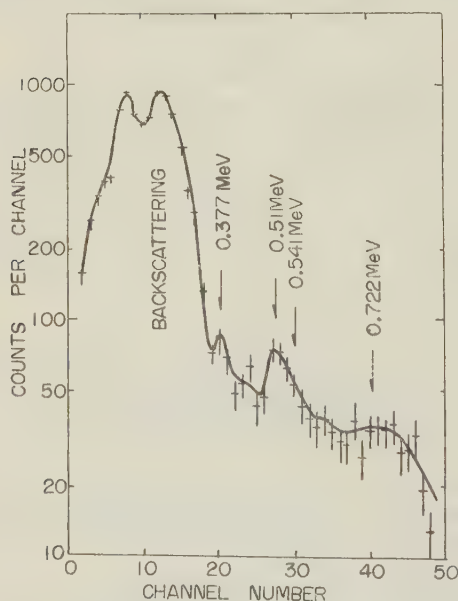


Fig. 1. Coincidence spectrum of the gamma rays from Ti^{45} . The main contribution to the broad peak may come from the backscattering of the annihilation radiations.

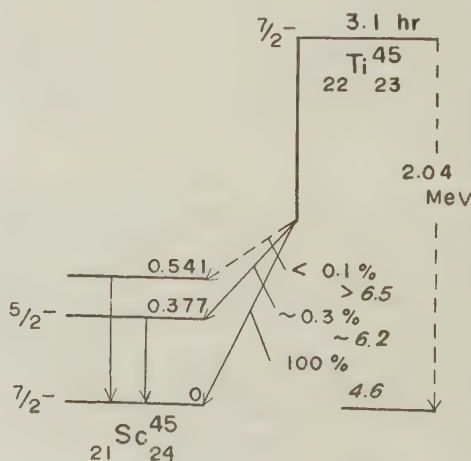


Fig. 2. Proposed decay scheme of Ti^{45} .

† Now at Department of Physics, Tokyo University, Bunkyo, Tokyo.

Since the configuration of the first excited state of almost all the nuclei which have the $7/2^-$ ground state is $5/2^-$, the 0.377-Mev state of Sc^{45} is expected to be $5/2^-$. The ground state of Ti^{45} is reasonably predicted as $7/2^-$ from the experimental $\log ft$ values obtained above. This assignment is confirmed by the fact that the transitions to the 0.54-Mev and the higher levels of Sc^{45} are very weak and hardly detectable. The above predicted decay scheme is shown in Fig. 2.

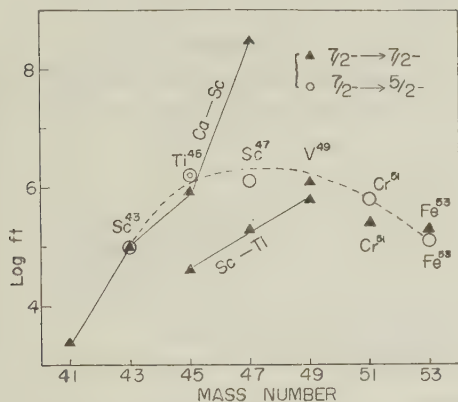


Fig. 3. Systematics of $\log ft$ values for nuclei with $(f_{7/2})^n$ configurations.

The $\log ft$ values for the beta decay of the $7/2^-$ (parent) $\rightarrow 7/2^-$ (daughter) and of the $7/2^-$ (parent) $\rightarrow 5/2^-$ (daughter) are plotted in Fig. 3 for the odd-A nuclei with $(f_{7/2})^n$ configurations³⁾. In the Fig. 3, the values for the transitions of $\text{V}^{47} \rightarrow \text{Ti}^{47}$ and $\text{Mn}^{51} \rightarrow \text{Cr}^{51}$, are omitted because of their indefinite spin values. The double circle in the figure is that of the $\text{Ti}^{45} \rightarrow \text{Sc}^{45*}$ (the 0.377-Mev level). The $\log ft$ values increase systematically with the shell filling and after the half filling it shows systematic decrease for both types of transition of the $7/2^- \rightarrow 7/2^-$ and the $7/2^- \rightarrow 5/2^-$. Although the systematics is very poor, the present prediction for spins and parities of Ti^{45} and Sc^{45} is consistent with these systematics.

The authors wish to thank Professor H. Morinaga for suggesting the problem and for helpful discussions.

References

- 1) P. M. Windham, C. R. Gossett, G. P. Phillips and J. P. Schiffer: *Phys. Rev.* **103** (1956) 1321.
- 2) H. Morinaga and T. Kuroyanagi: *Nuclear Instruments and Methods* **6** (1959) 66.
- 3) K. Way, R. W. King, C. L. McGinnis, R. van Lieshout: *Nuclear Level Schemes A=40-A=92*, U. S. A. E. C. TID-5300 (1955). K. Way, D. N. Kundu, C. L. McGinnis, R. van Lieshout: *Ann. Rev. Nucl. Sci.* vol. **6**, p. 129 (Annual Reviews Inc. Stanford 1956).

J. PHYS. SOC. JAPAN **15** (1960) 737-738

Angular Dependencies of Efficiencies for Sodium-Iodide Crystals

By Tadayoshi DOKE

Department of Physics, Rikkyo University

Atsushi NAKAMOTO, Yasukiyo TAKAMI,
Manabu HATTORI

*The Institute for Atomic Energy,
Rikkyo University*

and Shinji OKANO

The Institute of Physical and Chemical Research

(Received January 6, 1960)

To obtain the energy distribution of gamma rays from a widely spread source, it is necessary to know the dependencies of the detection efficiencies on the incident direction of gamma rays. We calculated the variations of the total detection efficiencies for various incident directions of parallel gamma rays, and obtained the efficiencies at the peak of the response for monoenergetic gamma rays (intrinsic peak efficiencies) using the calculated values of total detection efficiencies and peak-to-total ratio measured experimentally.

The calculations are based on the assumption that the probability of interaction of photon with the crystal is proportional to $(1 - \exp[-\mu(E)l])$, where $\mu(E)$ is the total absorption cross section for the incident photon of the energy E and l is

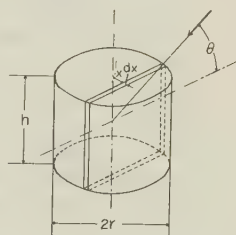


Fig. 1. Geometrical configuration.

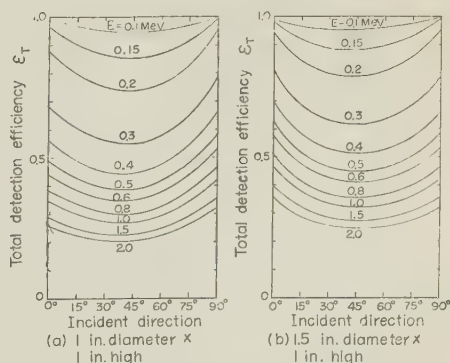


Fig. 2. Angular dependencies of total detection efficiencies for NaI(Tl) crystals.

the length traveled through the crystal. Also, the crystal was considered to consist of thin rectangular slices as shown in Fig. 1, and its efficiency was weighted by the number of photon received by the each slice normalizing total incident photon as unit, and then the efficiencies were integrated over the whole region of the crystal. The formula for the total detection efficiency $\epsilon_T(E, \theta)$ obtained by the above mentioned method was applied to three sodium-iodide crystals of different size: 1'' (diameter) $\times$ 1'' (height), 1.5'' $\times$ 1''. The efficiencies were computed with a Bendix Computer, every 15° between 0° and 90° and over the energy range from 0.1 Mev to 2 Mev. Values of the total absorption cross section were used from the table compiled by

K. Siegbahn¹⁾. The estimated error in calculations is less than 2% for all energy range. The result of the calculations are shown in Fig. 2. From the spectra of Cs-137 and Zn-65 obtained experimentally, we confirmed that the peak-to-total ratios of these crystals remained almost constant for incident direction of gamma rays. Therefore, it is considered that the variation of the peak-efficiency for incident direction of gamma ray is nearly equivalent to variation of the total detection efficiencies for these crystal sizes.

Reference

1) K. Siegbahn: *Beta and Gamma-Ray Spectroscopy* (Intersci. Publ., New York, 1955).

Errata

Volume Magnetostriction of Cobalt-nickel Alloys

By Takejiro KANEKO
J. Phys. Soc. Japan **15** (1960) 463

Page	Column	Line	Wrong	Corrected
465	left	eq. (2)	$T(\partial\sigma/\partial T)$	$T\rho(\partial\sigma/\partial T)$ (ρ : density)
"	right	5	$T(\partial I/\partial T)$	$T\rho(\partial\sigma/\partial T)$

Maxwell's Formula for Three-Dimensional and Large Deformation

By Wataru SEGAWA
J. Phys. Soc. Japan **15** (1960) 339

Page	Column	Line		Should be read
340	left	27	$x^i_{,\lambda} x^i_{,\lambda}$	$x^i_{,\lambda} x^j_{,\lambda}$
340	left	35	$x^j_{,\lambda} x^j_{,\mu}$	$x^i_{,\lambda} x^j_{,\mu}$
340	left	46	$x^j_{,\alpha} x^j_{,\beta}$	$x^i_{,\alpha} x^j_{,\beta}$
341	left	12	equations	equation contains
342	right	14	$= \frac{d}{d\alpha}$	$= \frac{1}{2} \frac{d}{d\alpha}$
343	left	18	defined	defined by

PROGRESS OF THEORETICAL PHYSICS

CONTENTS

Progress of Theoretical Physics

Vol. 23, No. 1, January 1960

Quantum Mechanics in Curved Space-Time	S. P. MISRA..	1
On a Possible Generalization of Quantum Mechanics	Tadashi KANEKO..	17
Measurement in Quantum Mechanics	Hitoshi WAKITA..	32
A Formal Theory of Collective Behavior	Kazuo HIROIKE..	41
Dependence of p - p Scattering Parameters on Phase Shifts	B. P. NIGAM..	61
On the Derivation of the Optical Potential in Infinite Nuclear Matter	B. JANCOVICI..	76
Bremsstrahlung in High Density Media at High Energies	Y. H. ICHIKAWA and M. YAMAMOTO..	81
Spin-Orbit Splitting and Tensor Force. I	Tokuo TERASAWA..	87
Electron Spin Resonance of Mn^{++} Ion in Ionic Crystals	Jun KONDO..	106
Spin-Orbit Splitting and Tensor Force. II	A. ARIMA and T. TERASAWA..	115
A Field Theoretical Investigation of Multiple Meson Production. I — <i>Pion-Nucleon Collisions</i> —	K. KOBAYAKAWA and T. IMAMURA..	137
Direct Capture of Slow Neutrons by the Nuclear p States	H. MORINAGA and C. ISHII..	161
Letters to the Editor:		
Meson Theoretical Potential and Nuclear Properties	T. SASAKAWA..	168
Possibility for or against the Existence of a Neutral Scalar Meson	K. IGI..	170
Polarization of Proton Scattered from Li^6 , Be^9 and B^{11}	Y. SAKAMOTO and T. TAKEMIYA..	172
Theory of Classical Fluids: Hyper-Netted Chain Approximation. IIIa — <i>A New Integral Equation for Pair Distribution Function</i> —	T. MORITA..	175
The New Viewpoint of the High Energy Elastic Scattering of Nucleons from Nuclei.....	T. SASAKAWA..	177
A Variation Principle in the Theory of Transport Phenomena	H. NAKANO..	180
A Variation Principle for Calculating General Susceptibility Tensors	H. NAKANO..	182
On the High Energy Protons Inelastically Scattered from C^{12} and O^{16}	Y. SAKAMOTO..	183
Ground State of a System Consisting of Two Oppositely Charged Particles in Coulomb Field.....	M. INOKUTI, K. KATSUURA and H. MIMURA..	186
Electric Multiple Transitions in $D(\gamma p)n$ Reaction at High Energy....	M. MATSUMOTO..	188
A Note on the Polarizations for p - He^3 and p - T^3 Scattering	Y. SAKAMOTO and T. TAKEMIYA..	190
On the Charge Distribution of the Proton	K. HIDA, N. NAKANISHI and T. SHIOZAKI..	192
Proton-Antiproton Annihilation and Nucleon Structure.....	S. MINAMI..	194
Contents of Journ. Phys. Soc. Japan, Vol. 14, No. 12.....		i~ii

Progress of Theoretical Physics

Vol. 23, No. 2, February 1960

A Method of Approximate Second Quantization in the Theory of Super- conductivity	Zygmunt GALASIEWICZ..	197
---	-----------------------	-----

Removal of Ghost-Pole and Unitarity of S -Matrix	
.....T. OGIMOTO and K. YAMAMOTO..	218
Selection Rules for Interaction Types in Quantum Field Theory	Shoji OZAKI..
Theory of Line-Shapes of Interband Magneto-Optical Absorption in Semi-	
conductors	T. OHTA, M. NAGAE and T. MIYAKAWA..
Contribution from the Three-Pion State to the Axial Vector Coupling Constant	
in β -Decay	Y. FUJII and S. FURUICHI..
On the Redundant Solutions of the Bethe-Salpeter Equation	
..... Y. OHNUKI, Y. TAKAO and H. UMEZAWA..	273
A Note on the Ordinary and Anomalous Thresholds in Perturbation Theory	
..... Noboru NAKANISHI..	284
Coupling Types and Strengths of the Y - N - K Interactions	
.....R. SUGANO and A. KOMATSUZAWA..	287
Propagation of Shock Waves in Inhomogeneous Gases. I	
..... Y. ÔNO, S. SAKASHITA and H. YAMAZAKI..	294
On a New Approach to Cosmology. II— <i>The Problem of Local Gravitation</i> —	
.....H. NARIAI and Y. UENO..	305
On the Electromagnetic Structure of Nucleons and Their Mass Difference..	
..... Y. KATAYAMA, M. TAKETANI, S. RAGUSA and D. R. de OLIVEIRA..	328
Mass Difference between the Sigma Hyperons	A. H. ZIMERMAN..
Two-Nucleon Potential with the "One-Pion-Exchange Tail". II.....	
....T. HAMADA, J. IWADARE, S. OTSUKI, R. TAMAGAKI and W. WATARI..	366
Letters to the Editor:	
Effects of the Weak Interaction on the Hydrogen Energy Levels	
.....S. GOTO and S. MACHIDA..	372
Spontaneous Magnetization, a Generalized Square Lattice	
..... I. SYOZI and S. NAYA..	374
A Note on the Phenomenological Theory of Unstable Particles	
.....A. Krzywicki and J. Szymanski..	376
The Role of Electron-Phonon Interaction in the Impurity Conduction	
of Semiconductors	Y. TOYOZAWA..
The Spatial and Time-Fluctuation of Coulomb Energy in the Low	
Concentration Impurity Conduction	Y. TOYOZAWA..
On the Polarization of High Energy Nucleon Elastically Scattered	
from Light Nuclei	Y. SAKAMOTO..
Integral Equation for Pair Distribution Function	
.....T. MORITA and K. HIROIKE..	385
On the Collective Excitation of Spherical Nuclei	
.....M. KOBAYASHI and T. MARUMORI..	387
Errata:	
On the Theory of Cooperative Phenomena (Vol. 11, p. 476)..	S. KATSURA..
Contents of Journ. Phys. Soc. of Japan, Vol. 15, No. 1	i
Contents of Suppl. Prog. Theor. Phys., No. 11 and No. 12	ii

Price	\$ 1.25 per copy
	\$ 15.00 per year (postage inclusive)
Annual dues for foreign members (individual subscribers)	\$ 12.00 (postage inclusive)
" for foreign members of the Physical Society of Japan	\$ 10.00 (postage inclusive)
Application for members, subscriptions and orders for back numbers should be sent, directly or through book-dealers, to	
The Publication Office	

in

Yukawa Hall, Kyoto University, Kyoto, Japan

.

The Reactions $\text{Li}^7(p, n)\text{Be}^7$, $\text{B}^{11}(p, n)\text{C}^{11}$ and $\text{Al}^{27}(p, n)\text{Si}^{27}$ at 8 to 14 MeV

By Kazuo HISATAKE,** Yoshihide ISHIZAKI,* Akira ISOYA,*
Teruo NAKAMURA,*** Yoshihiro NAKANO,**** Bunsaburo
SAHEKI,***** Yoshio SAJI* and Kazunori YUASA*****

*Institute for Nuclear Study, University of Tokyo,
Tanashi-machi, Tokyo*

(Received November 6, 1959)

The (p, n) reactions for lithium, boron and aluminium targets were studied by using two kinds of proton-recoil, fast-neutron spectrometers. One is an addition type originated by Calvert, Jaffe and Maslin, the other is a type with hydrogen gas radiator.

The angular distributions of $\text{Li}^7(p, n)\text{Be}^7$ neutrons corresponding to the ground and the 0.43 MeV excited states doubles at 8.1 to 14.1 MeV of proton energies and corresponding to the 4.65 MeV excited state of Be^7 at 14.1 MeV of proton energy were obtained. Using the activation method, the excitation curve of this reaction was observed with 15 MeV proton beam.

The angular distributions of neutrons from the reaction $\text{B}^{11}(p, n)\text{C}^{11}$ (the ground state) at 8.1 to 14.1 MeV and from the reactions $\text{Al}^{27}(p, n)\text{Si}^{27}$ (the ground and the excited states) at 14.1 MeV of proton energy were also observed.

The theory of Austern, Butler and McManus does not agree with the obtained results in the case of the reaction $\text{B}^{11}(p, n)\text{C}^{11}$, but agrees with that in the reaction $\text{Al}^{27}(p, n)\text{Si}^{27}$. It was observed that, for the reaction $\text{B}^{11}(p, n)\text{C}^{11}$, the isotropic parts of the angular distributions of neutrons became larger as the incident proton energies decreased and, in the cases of the reactions of $\text{Li}^7(p, n)\text{Be}^7$ and $\text{B}^{11}(p, n)\text{C}^{11}$, the angular distributions of neutrons showed large variations for the different proton energies.

§ 1. Introduction

The experimental data about (p, n) reactions are less than those about the other reactions because of the technical difficulties of neutron detection. Only a few works have been carried out to obtain the angular distributions of neutrons from (p, n) reactions. On the other hand, Austern, Butler and McManus¹⁾ introduced an interesting theory with regard to the angular distribution of protons from (n, p) reactions. Since the (p, n) reaction is a reverse process to the above mentioned reaction, their theory can be applicable to this reaction.

Batchelor and Marrison²⁾ studied the angular

distribution of the $\text{Li}^7(p, n)\text{Be}^7$ neutrons at 2.5 to 2.9 MeV with a fast neutron spectrometer. They measured the angular distributions of the two neutron groups corresponding to the ground and the first excited states of Be^7 respectively. However, observations were performed at only four angles of neutron emission. Recently Krasichov, Linev, Ribakov and Sidorov³⁾ obtained the angular distributions of the neutrons from the Li^6 and $\text{Li}^7(p, n)$ reactions at 9.6 MeV by means of a time-of-flight method and observed that the total cross section of the $\text{Li}^6(p, n)\text{Be}^6$ reaction was only 5% of that of the $\text{Li}^7(p, n)$ reaction. Kalinin, Oglobin and Petrov⁴⁾ obtained the excitation curves of the $\text{Li}^7(p, n)\text{Be}^7$ and $\text{B}^{11}(p, n)\text{C}^{11}$ reactions by a stack foil method at 12.2 MeV.

Ajzenberg-Selove, Johnson and Rubin⁵⁾ studied the neutrons from the $\text{B}^{11}(p, n)\text{C}^{11}$ reaction at 7 MeV with emulsion. They obtained the

* Institute for Nuclear Study, University of Tokyo.

** Tokyo Institute of Technology.

*** Univ. of Kyoto.

**** Hokkaido Gakugei Univ.

***** Konan Univ.

neutron energy spectra at four different angles.

Adelson⁶⁾ observed the neutron energy spectra from the $\text{Al}^{27}(p, n)\text{Si}^{27}$ reaction at three different angles for 31.5 MeV of incident proton energy, with a bubble chamber. However, because of the poor resolution each level could not be separated.

The purpose of the present work is to obtain the angular distributions of the neutrons from the $\text{Li}^7(p, n)\text{Be}^7$, $\text{B}^{11}(p, n)\text{C}^{11}$ and $\text{Al}^{27}(p, n)\text{Si}^{27}$ reactions for various incident proton energies from 8.1 to 14.1 MeV. The energy dependencies of the angular distributions were obtained and the theory of Austern, Butler and McManus was compared with our experimental results. In the case of the angular distribution of the $\text{Al}^{27}(p, n)\text{Si}^{27}$ neutrons, the experiment was done only at 14.1 MeV.

§2. Fast Neutron Spectrometers

For fast neutron detection, two different types of spectrometers were successively used. The one is an addition type as shown in Fig. 1, which has been originated by J. M. Calvert, A. A. Jaffe and E. E. Maslin.⁷⁾ In this spectrometer two scintillators are mounted on the axis of the incident neutron beam so that the recoil protons produced in the first scintillator, which is an anthracene crystal, complete their ranges in the second, which is of sodium iodide. The anthracene crystal used was a disk of 16 mm in diameter and 2 mm in thickness. The arrangement of the spectrometer is such that only those recoil protons leaving the anthracene crystal with a small angle to the direction of incident neutrons be accepted by the second crystal. The recoil protons getting almost all of the

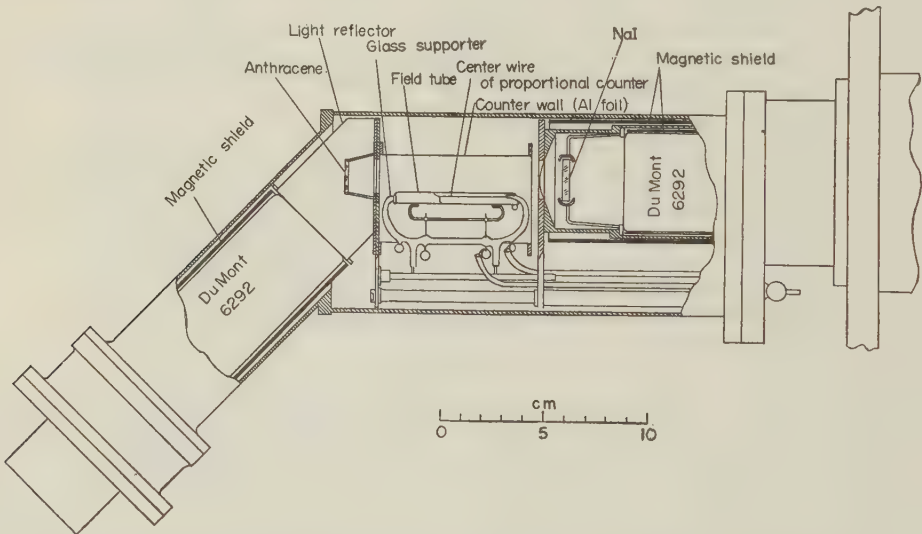


Fig. 1. Construction of proton recoil fast neutron spectrometer of addition type.

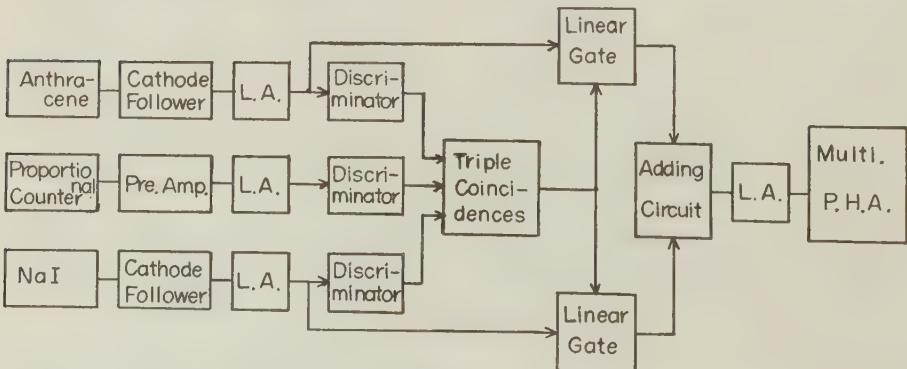


Fig. 2. Block diagram of electronic circuit used with the fast neutron spectrometer of addition type.

incident neutrons produce simultaneous pulses at both crystals and these pulses be suitably amplified separately and be added with the appropriate gain ratio.

The block diagram shown in Fig. 2 illustrates the electronic functions. The proportional counter, which is used for triple coincidence connection with two scintillators, serves to identify the recoil protons and to eliminate the background caused by the intense flux of γ -rays and undue neutrons. The counter has a field tube of the type described by Jhonson and Trail⁸⁾ and also has separators of thin aluminium foil at both sides, which isolate the counter from the light originating in the scintillators. Since the anthracene crystal can be as thick as the range of the recoil protons from the neutron groups being studied, the present spectrometer should have higher efficiency for neutron detection than the neutron spectrometers with thin radiators, without too much reduction of energy resolution. Actually, the efficiency of this type for 10 MeV neutrons is about six times larger than that of the gas radiator type as is mentioned next, and the energy resolution is 5 to 7 percents.

In spite of the above mentioned excellence in this type, it needs trial-and-error adjustment, which takes time, to determine the appropriate adding ratio. Moreover, small drifts in electronics, mostly in the part of photomultipliers, caused serious loss in energy resolution and measurement could not be continued for a long time, (for ten minutes in some case), without any readjustment.

Then, most measurements were performed

by the following spectrometer of the second type except for the aluminium and lithium reaction at 14.1 MeV.

The second type is a kind of the proton recoil fast neutron spectrometer with gas radiator. The construction was reported by one of the authors⁹⁾. Hydrogen gas is used as a radiator, because the largest numbers of hydrogen atoms can be contained there for the constant stopping power of protons. The hydrogen gas of 6 kg/cm² in pressure was filled in a steel cylinder of 5 cm in length and of 2 cm in diameter with a hemispherical cap.

Three proportional counters, which were connected in coincidence with the scintillator of sodium iodide crystal, were set between the radiator and the scintillator. It was found that the use of multiple proportional counter was very useful to eliminate the background pulses.

The sodium iodide crystal was mounted at some distance apart from the photomultiplier to avoid the effect of the non-uniform sensitivity of the photocathode. The defining aperture of the scintillator cavity was either 16 or 13 mm in diameter. The distance between the radiator and the scintillator was devised to be variable from 7 cm to 10 cm.

The total energy resolution was estimated to be about 3%. The obtained value in the best condition was of the same order, but in many cases this condition was hard to be obtained, probably on account of drift of the photomultiplier gain.

The efficiency of this spectrometer was estimated to be 1.34×10^{-5} for 10 MeV

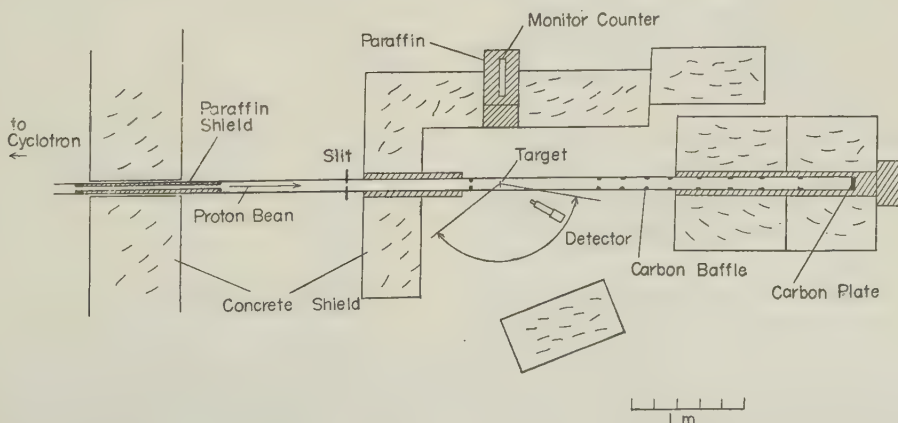


Fig. 3. Experimental arrangements.

neutrons, where the defining aperture of the scintillator cavity was 16 mm in diameter and the distance between the radiator and the scintillator was 82 mm. The absorption of neutrons in the matters which construct the walls of the target chamber and of the hydrogen gas container was corrected by assuming that the absorption coefficient obtained from the total cross section of neutrons in those materials.

§ 3. Experimental Arrangements

The present work has been performed by using the 160 cm variable energy cyclotron at the Institute for Nuclear Study, Univ. of Tokyo.

The arrangement of experimental equipments is shown in Fig. 3. The proton beam is suitably focussed on the target by means of the quadrupole magnets and is defined by the graphite slit at some distance from the target. The target chamber is made of a thin walled steel pipe and is protected against undue neutrons and γ -rays by heavy shields of paraffin and concrete blocks. A long pipe, 2 meters in length, which is isolated electrically follows the target chamber and has a graphite stopper to the beam at the end and also has many graphite rings inside it to protect the inner surface of the pipe against direct bombardment by protons scattered from the target. This long pipe also plays the role of the beam current monitor.

The spectrometer can be rotated around the target from 8° to 140° to the beam direction with a variable distance from the target.

As a neutron monitor, a BF_3 proportional counter is placed at the 90° to beam direction. In order to increase the efficiency for high energy neutrons, its front surface is covered with a thick layer of paraffin and a cadmium plate.

The beam current was 0.3 to 1.5μ amp., and the beam spot on the target is 2 to 8 mm in width and 15 mm in height. The background at the neutron spectrometer was negligibly small.

Several targets were prepared as follows: 40 microns aluminium foil was used for aluminium target. For lithium target, natural lithium metal was thinned down by a roller with oil into about 100 microns in thickness and after washing by naphta solvent it was

taken in the target chamber as soon as possible. For the boron experiment, natural boron powder mixed with lacquer was stretched on thin maylor foils. The exact quantity of boron was determined by chemical analysis.

§ 4. Results

$\text{Li}^7(p, n)\text{Be}^7$ Reaction

Firstly, considerable effort was made to separate the two neutron groups corresponding to the ground and the first excited states of Be^7 . However, complete separation was not able to be obtained because of the too small energy difference (430 KeV) for the resolution of our spectrometer. But in some cases, the separated feature of the doublet were obviously obtained as shown in Fig. 4.

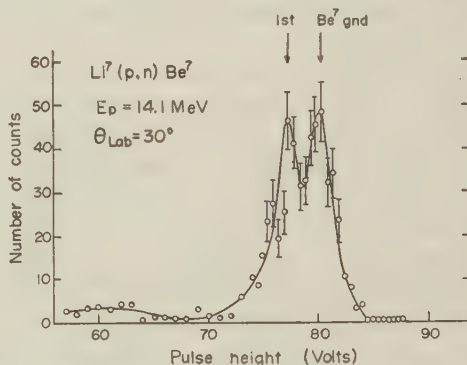


Fig. 4. Neutron energy spectrum of the $\text{Li}^7(p, n)\text{Be}^7$ reaction at 30° of lab. angle for proton energy of 14.1 MeV.

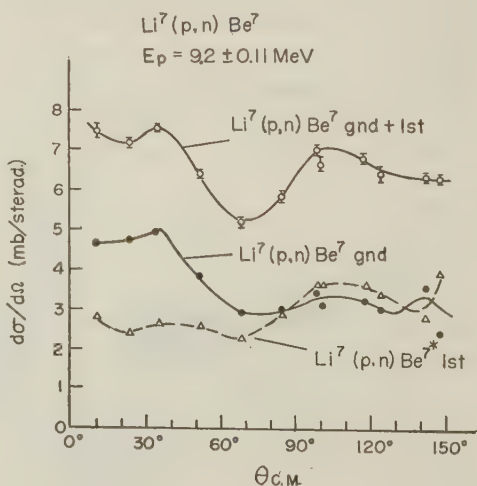


Fig. 5. Rough estimation with regard to angular distribution of $\text{Li}^7(p, n)\text{Be}^7$ neutrons corresponding to the ground and the first excited states of Be^7 at 9.2 MeV.

From those results, the two neutron groups of the doublet seem to have comparable intensity over the whole energy region investigated in this work. A rough estimation of the relative intensity at 9.2 MeV is shown in Fig. 5.

Fig. 6 shows an example of neutron energy spectrum from the $\text{Li}^7(p, n)\text{Be}^7$ reaction. The background due to neutrons from the parts other than the target seems to be negligible. The contributions from the $\text{Li}^6(p, n)\text{Be}^6$ reaction may be negligible, because of its low natural abundance (7.4%) and yield, which

has been observed³⁾ to be only 5% of the other.

The angular distributions of the combined neutron groups (corresponding to the ground and the first excited states) from the reaction $\text{Li}^7(p, n)\text{Be}^7$ at the various proton energies are shown in Fig. 7. It is found that the feature of the angular distribution varies greatly as the incident proton energy varies. However, since two neutron groups were not completely separated and they showed different angular distributions as shown in Fig. 5, the comparison with the theory has not been done.

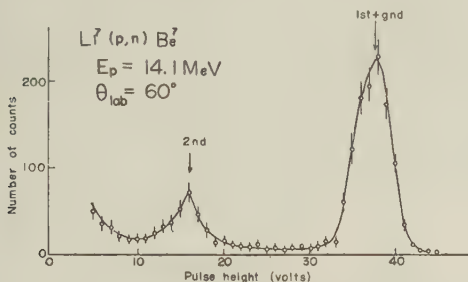


Fig. 6. Energy spectrum of neutrons from the $\text{Li}^7(p, n)\text{Be}^7$ reaction at 60° of lab. angle for proton energy of 14.1 MeV.

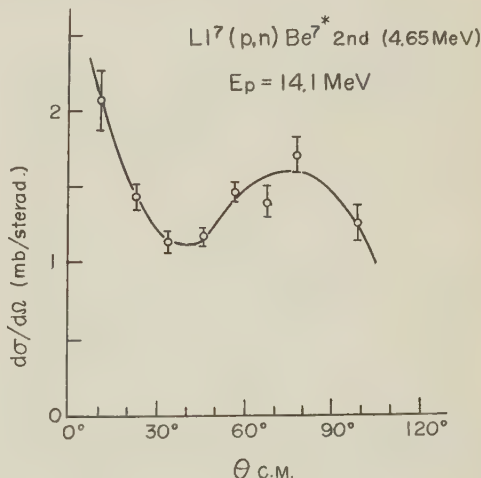


Fig. 8. Angular distribution of neutrons from the reaction $\text{Li}^7(p, n)\text{Be}^7^*$ (4.65 MeV excited state) at 14.1 MeV.

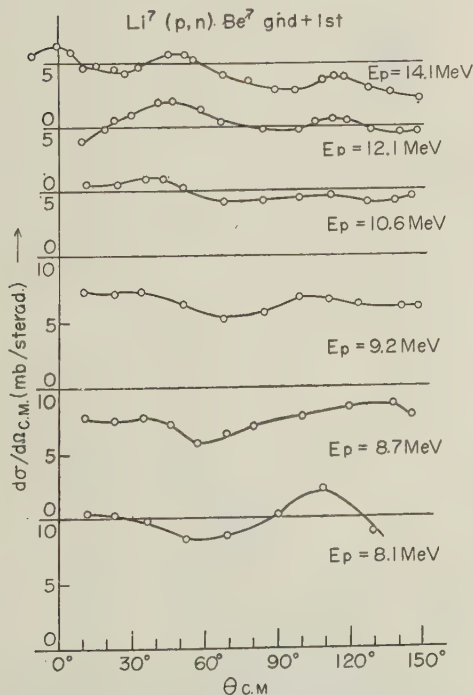


Fig. 7. Angular distributions of the $\text{Li}^7(p, n)\text{Be}^7$ combined neutron groups corresponding to the ground and the first excited states of Be^7 at 8.1 to 14.1 MeV of proton energies.

The angular distribution of neutrons corresponding to the second excited state (4.65 MeV state) of Be^7 was also observed at 14.1 MeV of proton energy as shown in Fig. 8.

Moreover, the total cross section of the $\text{Li}^7(p, n)\text{Be}^7$ reaction as a function of incident proton energy has been investigated. The Be^7 nucleus decays to the ground and the 0.477 MeV excited states of the Li^7 nucleus by electron capture with the half life of 53 days and the branching ratio to the excited state is about 10%. In the present experiment, the 477 KeV γ -rays accompanying to decay of the excited state was measured to obtain the total cross section.

Firstly, several lithium foils were bombarded by proton beam of different energies one by one. The activity of each foil was measured by sodium iodide crystal with

dimensions of $1''(\text{diameter}) \times 1''$, $1 \frac{1}{2}''(\text{diameter}) \times 1''$ and $5''(\text{diameter}) \times 4''$. On the other hand, the stack foil method was also used. In this case, the activities were measured by a "well type" sodium iodide scintillator.

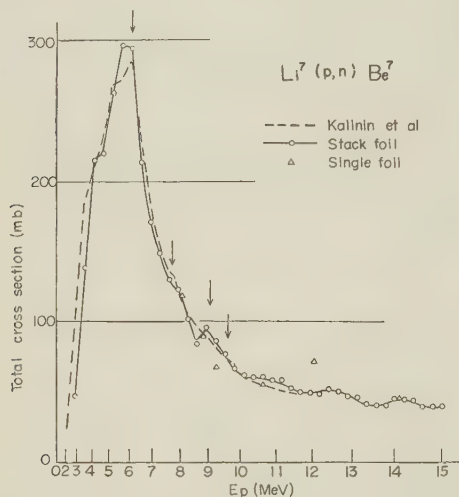


Fig. 9. Excitation curves of the $\text{Li}^7(p, n)\text{Be}^7$ reaction. Arrows show the levels of the compound nucleus Be^8 observed by Kalinin et al.

The results are shown in Fig. 9. In this figure, the results obtained by Kalinin, Oglobin and Petrov⁴⁾, using the stack foil method, are also represented by the dashed curve. All the absolute values of the total cross sections are normalized to the value obtained by our single foil method. The values obtained by Kalinin et al. are about 50% larger than ours. Except for this point, those show good agreement with each other and the levels of the compound nucleus Be^8 observed by Kalinin et al. were also confirmed. In this figure, some new broad resonances seemed to be found in the energy region higher than that of Kalinin et al.

$\text{B}^{11}(p, n)\text{C}^{11}$ Reaction

The angular distributions of neutrons from the $\text{B}^{11}(p, n)\text{C}^{11}$ reaction at various proton energies were studied. Fig. 10 shows an energy spectrum of neutrons for the proton energy of 14.1 MeV. and Fig. 11 shows the angular distributions of the neutrons corresponding to the ground state of C^{11} at various proton energies. In order to compare with the theory introduced by Austern, Butler and McManus, analysis of the experimental

results was done.

Their equation is given as:

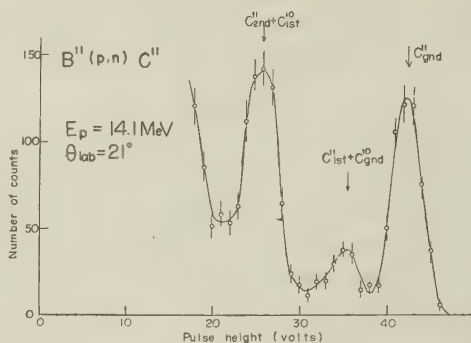


Fig. 10. Neutron energy spectrum of the $\text{B}^{11}(p, n)\text{C}^{11}$ reaction at 21° of lab. angle for proton energy of 14.1 MeV.

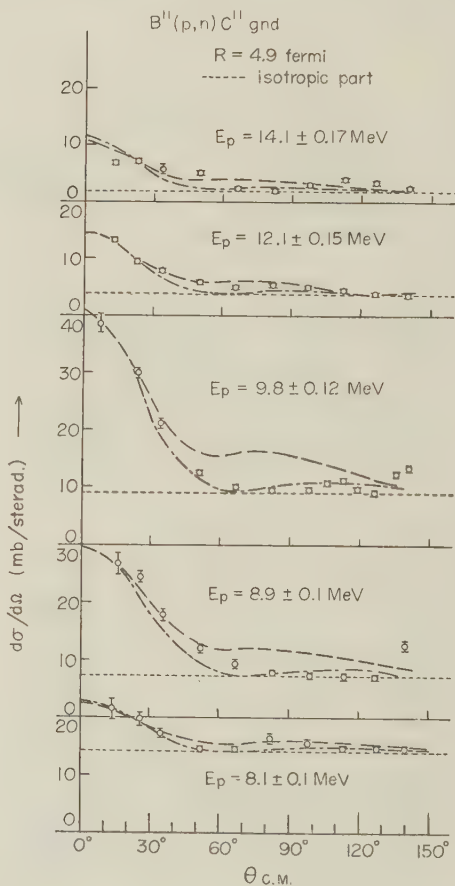


Fig. 11. Angular distributions of neutrons from the $\text{B}^{11}(p, n)\text{C}^{11}$ (ground state) reaction at 8.1 to 14.1 MeV of proton energies. The dashed curves represent the calculations following to the theory of Austern, Butler and McManus and the dash- and dotted curves represent the calculations with only j_0 term.

$$\sigma(\theta) \propto \sum_l C_{in\ l\ p}^2(l, 0; 0, 0) \{j_l(kR)\}^2$$

where, $C_{in\ l\ p}$ is Clebsh-Gordan coefficient. In the present case, the form becomes as follows:

$$\sigma(\theta) \propto \frac{1}{3} \{j_0^2(kR) + 2j_2^2(kR)\}.$$

The isotropic parts of the angular distributions were subtracted from the experimental values and compare with the theory, as was done by Evance and French¹⁰⁾ in their analysis of the (d, p) reaction. The results calculated are represented with the dashed curves in Fig. 11. The agreement between the experimental results and the calculations is not good. If the second term in the calculation, the j_2 term, is neglected, the dash-and dotted curves are obtained. It is noticed that, the dash- and dotted curves, which contain only j_0 term, rather agree with the experimental curves.

$Al^{27}(p, n)Si^{27}$ Reaction

The angular distribution of neutrons from

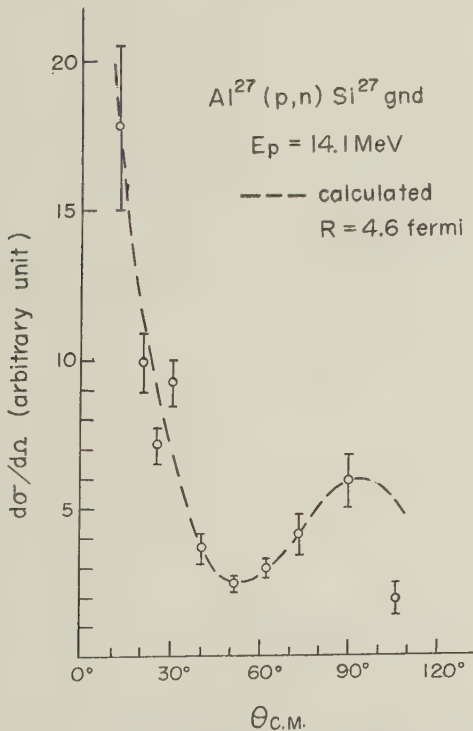


Fig. 12. Angular distribution of neutrons from the $Al^{27}(p, n)Si^{27}$ (ground state) reaction at 14.1 MeV of proton energy. The dashed curve represents the calculation following to the theory of Austern, Butler and McManus.

the $Al^{27}(p, n)Si^{27}$ reaction was also investigated only at 14.1 MeV. Because of the weakness of neutron intensity, the results contain large errors. The angular distribution of neutrons corresponding to the ground state of Si^{27} is shown in Fig. 12. The absolute cross section of this reaction could not be exactly estimated, but it is sure that this cross section is an order of tenth of that of the $B^{11}(p, n)C^{11}$ reaction.

Applying the equation of Austern, Bulter and McManus in this case, the differential cross section is represented as follows:

$$\sigma(\theta) \propto j_0^2(kR) + \frac{5}{14} j_2^2(kR) + \frac{72}{35} j_4^2(kR).$$

The dashed curve in this figure shows the calculation. The agreement of the experimental results with the calculated ones are very good.

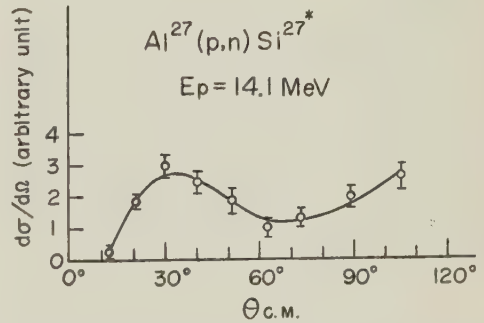


Fig. 13. Angular distribution of neutrons from the $Al^{27}(p, n)Si^{27*}$ reaction at 14.1 MeV of proton energy.

Fig. 13 shows the angular distribution of neutrons corresponding to the excited states (probably the first and the second excited states).

§ 5. Discussions

Comparing the obtained results with the theory of Austern, Butler and McManus, it is found that the angular distributions of neutrons from the $B^{11}(p, n)C^{11}$ reaction do not show very good agreement with the theory, but on the other hand, the angular distributions of the neutrons of the $Al^{27}(p, n)Si^{27}$ reaction agree comparatively well. While, one of the authors⁹⁾ has shown that disagreement between the experimental results and the theory is larger in the case of the $Be^9(p, n)B^9$ reaction. Although the

separation of the two neutron groups is not complete, the disagreement in the $\text{Li}^7(p, n)\text{Be}^7$ reaction seems to be clear. From these facts it may be concluded that the assumption of the above mentioned theory cannot be applicable to such lighter nuclei.

The angular distributions of neutrons from the $\text{B}^{11}(p, n)\text{C}^{11}$ reaction show that the isotropic parts become larger as the incident proton energy decreases. It is probably considered that in the lower energy region, the formation of a compound nucleus is more preferable than the direct process.

It is of interest that the angular distributions of the neutrons from the $\text{Li}^7(p, n)\text{Be}^7$ and $\text{B}^{11}(p, n)\text{C}^{11}$ reactions show large variations for the different incident proton energies, while that from the $\text{Be}^9(p, n)\text{B}^9$ reaction varies comparatively slowly as the proton energy varies as reported by one of the authors.⁹⁾

The results obtained by the activation method, show that the total cross section of the $\text{Li}^7(p, n)\text{Be}^7$ reaction has a broad resonance at 12.4 MeV of proton energy, while the angular distribution of neutrons has also similar feature at the proton energies near to the above, say, 12 MeV. Both the results are consistent with each other.

The disagreement of the absolute cross section of the $\text{Li}^7(p, n)\text{Be}^7$ reaction between the results observed by Kalinin et al. and the present work can not be explained. The error of our results are estimated to be less than 20%. It should be noticed that, both

the total cross sections of the $\text{Li}^7(p, n)\text{Be}^7$ reaction obtained by Kalinin et al. and us are not very exact, since the other processes, such that Be^7 decays also to He^3 and He^4 , may compete with the observed process especially in the high energy region not being measured by the activation method.

Acknowledgement

The authors wish to thank Prof. I. Nonaka for his encouragement and Dr. Kazuo Saito for his chemical analysis of the targets. Thanks are also due to the cyclotron operators and the members of the electronics and the chemistry divisions in the institute for their kind helps.

References

- 1) N. Austern, S. T. Butler and H. McManus: Phys. Rev. **92** (1953) 350.
- 2) R. Batchelor and G. C. Morrison: Proc. Phys. Soc. London **A**, **68** (1955) 1081.
- 3) A. A. Kurasichov, A. F. Linev, B. V. Ribakov and V. A. Sidorov: Atom. Energ. **5** (1958) 135.
- 4) C. P. Kalinin, A. A. Oglobin and Yu. M. Petrov: Atom. Energ. **2** (1957) 171.
- 5) F. Ajzenberg-Selove, G. D. Johnson and A. Ruhin: Phys. Rev. **103** (1956) 356.
- 6) H. A. Adelson: UCRL 8568 (1958).
- 7) J. M. Calvert, A. A. Jaffe and E. E. Maslin: Proc. Phys. Soc. London **A**, **69** (1955) 1017.
- 8) C. H. Johnson and C. C. Trail: Rev. Sci. Inst. **27** (1956) 468.
- 9) Y. Saji: J. Phys. Soc. Japan **15** (1963) 367.
- 10) N. T. S. Evans and A. P. French: Phys. Rev. **109** (1958) 1272.

Protons from the $p+d$ Breakup Reaction at Proton Energies of 14 MeV and 10 MeV

By Seishi KIKUCHI, Junpei SANADA, Shigeki SUWA, Izuo HAYASHI,
Keigo NISIMURA and Kiyoji FUKUNAGA*

Institute for Nuclear Study, University of Tokyo, Tanashi-machi, Tokyo

(Received December 15, 1959)

The energy spectra of the protons from the $p+d$ breakup reaction as a function of angle were measured for the incident proton energies of 13.9 MeV and 10.1 MeV, using a particle selecting counter telescope consisting of a three- or five- layer proportional counter for the energy loss measurement and of an NaI scintillation counter for the energy measurement. Each of the observed energy spectra shows a rather steep rise at the maximum energy followed by a slight shoulder at large angles at the incident proton energy of 14 MeV, while the energy spectra at small angles do not show such shoulder. For both energies, each of the spectra has a maximum in its low energy side.

§ 1. Introduction

The breakup of deuterons by nucleons is of interest since it represents the simplest nuclear reactions and it may give some informations on the nucleon-nucleon interaction.

This process has been examined theoretically by Bransden and Burhop¹⁾, and by Frank and Gammel²⁾. Recently Heckrotte and MacGregor³⁾ evaluated the effect attributed to the final state interaction of the two protons for the breakup neutron spectrum from the $p+d$ reaction, which was neglected in the calculations of Frank and Gammel, and explained the neutron spectrum from the $p+d$ reaction measured by Nakada and co-workers⁴⁾ which showed a peak at the upper end of its energy spectrum. There were some experimental works on the neutron spectrum from the $p+d$ reaction⁵⁾. But experimental informations on the protons from the $p+d$ reaction are rather scanty²⁾.

This paper reports the measurements of the spectrum of breakup protons when deuterium is bombarded with protons of energies of 13.9 MeV and 10.1 MeV.

§ 2. Experimental Arrangements and Procedures

A. General considerations

The experimental arrangements were almost the same as those described in detail previously^{6), 7)}.

The external proton beam of the INSJ 160 cm variable energy cyclotron was brought to the scattering chamber of 100 cm diameter through a pair of magnetic quadrupole lenses, a sector type magnetic lens, a pair of collimating apertures and several antiscattering apertures. At the center of the scattering chamber, a 15 cm diameter gas target chamber with a 25 micron thick mylar window, which was 1.6 cm high and extended to 290° of arc was located. On the turntable, a particle selecting counter telescope was placed to detect breakup protons.

The beam current collected on a Faraday cup was integrated by a 100 percent feedback type beam current integrator. And the energy of the incident beam was determined by the measurement of the proton range in aluminium, and was monitored with the signal from the proton resonance type magnetic flux meter installed in the above mentioned sector type focusing magnet.

The deuterium gas of 99% purity for target was obtained by the electrolysis from heavy water and by passing through a heated palladium tube.

B. The measurement of the whole energy distribution

For the measurement of the whole energy distribution of scattered particles, a three- or five- layer proportional counter was used only as a counter telescope to remove the background counts in the NaI scintillation counter due to neutrons and gamma rays.

* Department of Physics, Faculty of Science, University of Kyoto

The detector system and the block diagram of the counting electronics are shown in Fig. 1 and Fig. 2. A typical one of the pulse height distributions in the NaI counter is shown in Fig. 3.

C. Removal of recoil deuterons

In some part of the pulse height distributions measured as described in B, breakup protons were masked by the recoil deuterons due to the p - d elastic scattering. To estimate the breakup proton component in this part, the following methods were applied.

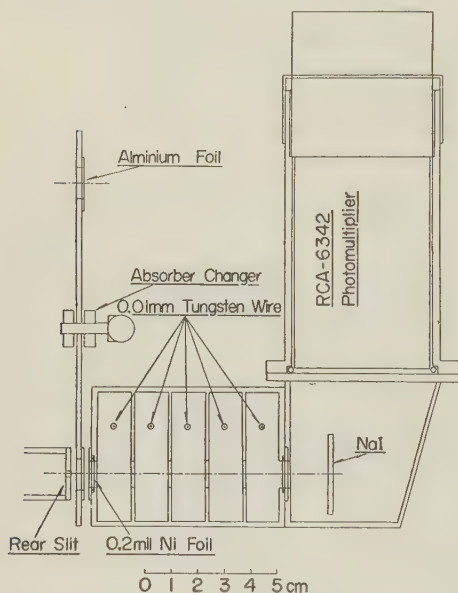


Fig. 1. Detector system consisting of a five-layer proportional counter and an NaI scintillation counter.

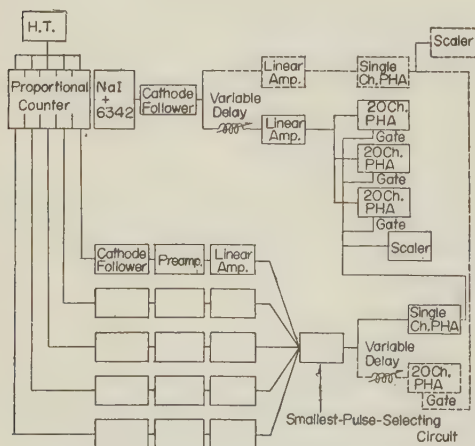


Fig. 2. Block diagram of the counting electronics. Dotted line indicates the case of the dividing method.

i) The three-layer proportional counter

Because of the mass dependence of the energy loss of charged particles in matter, it is possible to discriminate charged particles by their masses, if their energies and energy losses in matter are measured simultaneously with a sufficient accuracy. But to measure the energy loss, a counter of small stopping power is desirable in order that the energy measurement may not involve a large correction for the energy loss incurred in the energy loss measurement. And as shown by Landau⁶⁾, when charged particles traverse a thin lamina of matter, the frequency distribution of energy loss is a so-called Landau distribution with a broad full width and a pronounced high energy tail. There are a few attempts to obtain an accurate estimate of the mean energy loss of heavy charged particles using a device which has a small stopping power.

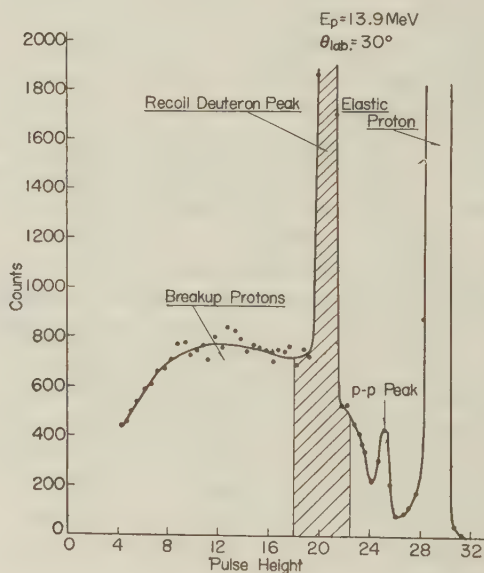


Fig. 3. Pulse height distribution in the NaI counter.

The methods using a multi-layer proportional counter, which were developed by Alikhanov et al.⁹⁾, seem promising. But in our case, the smallest pulse selecting method developed by Igo and Eisberg¹⁰⁾ was used for its simplicity. This method takes advantage of the steep rise of the low energy side of the Landau distribution to obtain an accurate estimate of the mean energy loss.

In this method the particles traverse N identical layers of the proportional counter

and the smallest of the N output pulses from these layers is considered as the mean energy loss.

In earlier stage we used a three-layer proportional counter for the energy loss measurement similar to that of Igo and Eisberg with gas pressure of 30 cmHg. The pulses from each layer were amplified by a preamplifier and a linear amplifier, and were fed to the smallest pulse selecting circuit which selected the smallest of the three pulses and passed it on. The resolution of this equipment which is seen from Fig. 4, was far more excellent than a single counter of the same total gas thickness, but was not sufficient to separate deuterons completely from protons whose pulse height in the NaI counter are equal to those of deuterons, and the energy spectrum of break-up protons covered with the recoil deuteron pulses could not be revealed all at once by means of anticoincidence with the proportional counter pulses corresponding to deuterons.

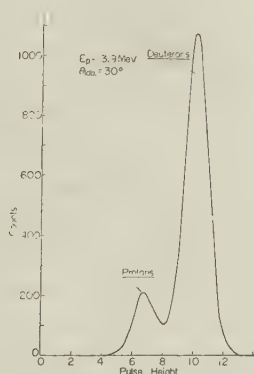


Fig. 4. Distribution of the smallest of the three-layer proportional counter pulses, coincident with the NaI pulses shown by the shaded area in Fig. 3.

We could not use the proportional counter at higher pressure, because it was undesirable to give a large disturbance to the pulse height distribution in the NaI counter. Then the following method was adopted to estimate the part of the breakup proton spectrum covered with deuteron pulses.

ii) The dividing method

The above-mentioned part of pulse height distribution in NaI counter was divided into several sections.

The pulses belonging to each section which were selected by a single channel pulse height

analyzer, gated the 20 channel pulse height analyzer which analyzed the output pulses from the smallest pulse selecting circuit of the three-layer proportional counter. From each of the pulse height distribution curves thus obtained, the yield of breakup proton component belonging to each divided section was obtained and the NaI counter pulse height distribution of breakup protons covered with the recoil deuteron pulses was estimated. The circuit diagram is shown in Fig. 2 by the dotted line. This method was used at the incident proton energy of 14 MeV.

iii) The anticoincidence method

In the pulse height distribution of the three-layer proportional counter, the Landau tail of small amount still remained. By some statistical calculations about the method of selecting the smallest of the pulses which have the Landau's frequency distribution, the usefulness of a five-layer proportional counter became clear. Then in later stage, we used a five-layer proportional counter which had nearly equal thickness with the three-layer proportional counter for the energy loss measurement. Using this counter, we succeeded in separating protons almost perfectly from deuterons in the region covered with deuteron pulses. The result is shown in Fig. 5.

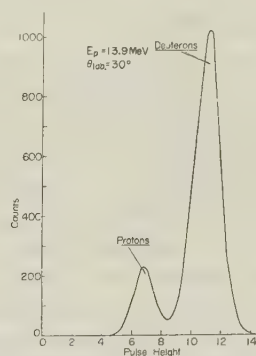


Fig. 5. Distribution of the smallest of the five-layer proportional counter pulses, coincident with the NaI pulses shown by the shaded area in Fig. 3.

Then we used the anticoincidence method to remove the deuteron pulses. The pulse height distribution in the NaI counter in anticoincidence with the output pulses from the smallest pulse selecting circuit, which were corresponding to the energy loss pulses of deuterons, were measured by the 20 channel

pulse height analyzers. The circuit diagram in this case was the same as in the case of the measurement of the whole energy distribution except that the 20 channel pulse height analyzers were gated by anticoincidence with the output pulses of the single channel pulse height analyzer instead of coincidence.

This method was used at angles of 10° , 20° , 30° and 40° at the proton energy of 10 MeV. And it was also used at 30° at the proton energy of 14 MeV in order to check the results of the dividing method described above.

iv) The absorber method

We used at the proton energy of 14 MeV also a method of shifting the position of deuteron pulses against proton pulses in the pulse height distribution in the NaI counter by introducing aluminium absorber of 75μ , 100μ , 200μ , or 250μ , properly in front of the counter telescope. This method was not accurate enough to deduce the energy distribution of breakup protons because it required a large correction to the results for the particle loss due to the multiple scattering in the absorber foils. But this method was useful in finding a general tendency of the shape of the part of the breakup proton spectrum, which otherwise was covered with the deuteron pulses and to check the results of the other procedures.

§ 3. Results and Discussion

After subtracting background counting and the elastic proton tail which have been discussed in the previous paper, the observed pulse height distribution at each angle at both incident proton energies was converted to the energy spectrum. The pulse height-energy conversion curves were completed by means of the pulse heights of protons, the energies of which were known by the kinematics, such as elastically scattered protons and protons scattered by a small amount of hydrogen gas contained in the target gas. In our detector the system, the cut-off energy for protons was 2.46 MeV and 2.25 MeV in the cases of the three- and five- layer proportional counters, respectively. Then, the energy distribution curves were corrected for the particle loss due to the multiple scattering in the front window and the gas of the proportional counter according to the method of Snyder and Scott⁽¹⁾. This correction was not large for energies larger than 5.5 MeV, but it exceeded 10% for energies

smaller than 5 MeV. The energy spectra as functions of angle and the angular distribution derived in this way are shown in Figs. 6, 7 and 8, smooth lines being drawn through the experimental points. The errors indicated are

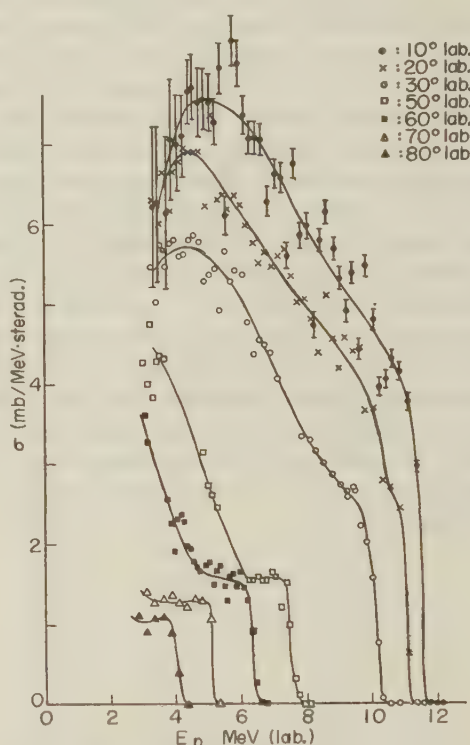


Fig. 6. Energy spectra of protons from $p+d$ breakup reaction at proton energy of 13.9 MeV.

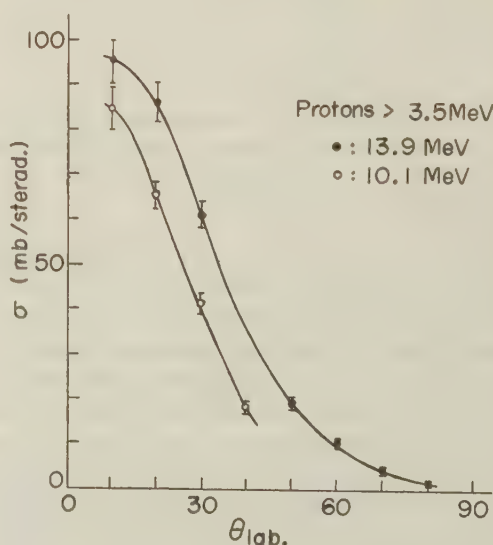


Fig. 7. Angular distributions of protons from $p+d$ breakup reaction at proton energies of 13.9 MeV and 10.1 MeV.

due to counting statistics and uncertainties in the corrections of particle loss due to the multiple scattering.

The error due to the uncertainty in the deuteron subtraction for the parts under the recoil deuteron peak was also considered. But the greater part of errors was due to uncertainties in the corrections of particle loss. We have not yet compared the present results with the theoretical predictions. The characteristics of our results are as follows:

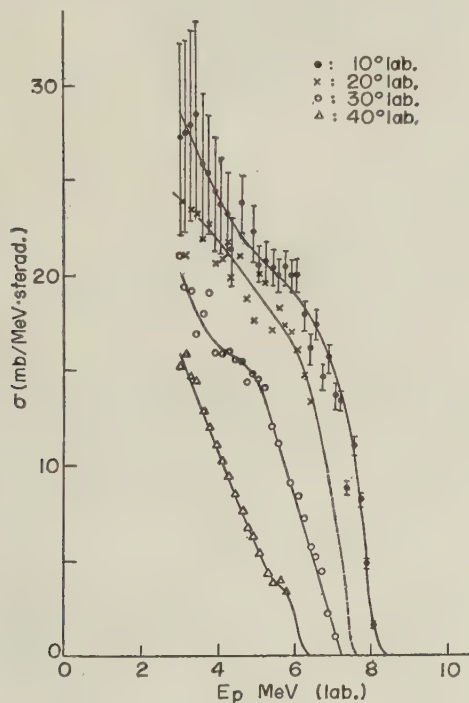


Fig. 8. Energy spectra of protons from $p+d$ breakup reaction at proton energy of 10.1 MeV.

Each of the breakup proton spectra at large angles shows a rather steep rise at the maximum energy followed by the slight shoulder for incident protons of 14 MeV, while the energy distributions at small angles do not show such shoulder. At both energies each of the distributions has a maximum in its

low energy side. We are preparing now a more accurate experiment at the same energy region.

Acknowledgements

The authors would like to thank the operating crew of the cyclotron, particularly Messrs. T. Karasawa, A. Suzuki and H. Ogawa. They also wish to express their thanks to Prof. I. Nonaka for his constant encouragement.

References

- 1) B. H. Bransden and E. H. S. Burhop: Proc. Phys. Soc. London A, **63** (1950) 1337.
- 2) R. Frank and J. Gammel: Phys. Rev. **93** (1954) 463.
- 3) W. Heckrotte and M. MacGregor: Phys. Rev. **111** (1958) 593.
- 4) M. P. Nakada, J. D. Anderson, C. C. Gardner, J. McClure and C. Wong: Phys. Rev. **110** (1958) 594.
- 5) A. F. G. Ferguson and G. C. Morrison: Nucl. Phys. **5** (1958) 41. L. Cranberg and R. K. Smith: Phys. Rev. **113** (1959) 587. N. A. Vlassov, S. P. Kalinine, B. V. Rybakov and V. A. Sidorov: *Comptes Rendus du Congres International de Physique Nucleaire*, Paris, (1958) 624.
- 6) J. Sanada: J. Phys. Soc. Japan **14** (1959) 1463. S. Kikuchi et al.: J. Phys. Soc. Japan to be published.
- 7) S. Kikuchi, J. Sanada, S. Suwa, I. Hayashi, K. Nisimura and K. Fukunaga: J. Phys. Soc. Japan to be published.
- 8) L. Landau: J. Phys. USSR **8** (1944) 201. K. R. Symon: Thesis, Harvard University (1948)
- 9) A. I. Alikhanov and V. Kharitonov: Doklady Akad. Nauk USSR **85** (1952) 295. G. P. Eliseiev, et al: Dokl. Akad. Nauk **90** (1953) 995. V. A. Lubimov, et al: Dokl. Akad. Nauk USSR **100** (1955) 883; **107** (1956) 233. A. I. Alikhanov, V. A. Lubimov and G. P. Eliseiev: Cern Symposium (1956) Proceedings
- 10) G. Igo and R. M. Eisberg: Rev. Sci. Instr. **25** (1954) 450.
- 11) H. S. Snyder and W. T. Scott: Phys. Rev. **76** (1949) 220.

Measurements of the Polarization in Proton-Helium Elastic Scattering

By Junpei SANADA*, Keigo NISIMURA*, Shigeki SUWA*, Izuo HAYASHI*,
Kiyoji FUKUNAGA**, Norio RYU*** and Masao SEKI****

Institute for Nuclear Study, University of Tokyo, Tanashi-Machi, Tokyo

(Received December 16, 1959)

The polarization of protons elastically scattered by helium was measured by the double scattering method. Incident proton or alpha-particle beam was obtained from the INSJ 160 cm variable energy cyclotron. Three interdependent measurements, in which the polarization product was equal to P_1P_2 , P_2P_3 or P_3P_1 , were made. The following results were obtained:

$$P_1(6.2 \text{ MeV}, 130.0^\circ) = 0.92 \pm 0.11$$

$$P_2(11.5 \text{ MeV}, 61.1^\circ) = -0.45 \pm 0.06$$

$$P_3(9.1 \text{ MeV}, 61.1^\circ) = -0.45 \pm 0.06,$$

where angles and energies are those in the center-of-mass system. Experimental values of the polarization agreed well to the values calculated by using phase shifts, which were obtained from the analysis of the angular distribution of the scattering cross sections.

§ 1. Introduction

Many experiments on the angular distribution of the elastic scattering of protons by helium have been performed and analysed in terms of phase shifts¹⁾. A few sets of phase shifts are found which are consistent with the observed differential cross sections. The polarization measurement may serve for the decision between them, because these sets of phase shifts give the different polarizations²⁾.

The fact that the virtual ground state and the first excited state of Li^9 form the inverted doublet of $P_{3/2}$ and $P_{1/2}$ was first established by the measurement of the polarization made by Heusinkveld and Freier³⁾ at the proton energy of about 3 MeV. In almost the same energy region, Scott⁴⁾ has made recently a more accurate measurement. Juveland and Jentschke⁵⁾ made a measurement at 5.32 MeV. The angular distribution of the polarization was taken at 10 MeV by Rosen and Brolley⁶⁾. Brockman⁷⁾ reported some results near 15 MeV.

The purpose of the present work is the extension of the experimental data of the polarization between 7 and 15 MeV. And it is a complement of the measurement of differential cross sections, which we have made recently⁸⁾.

§ 2. Experimental Method

External proton or alpha-particle beam from the INSJ 160 cm variable energy cyclotron was led to the double scattering chamber shown in Fig. 1. From the left-right ratio R of the scattered intensity in the second scattering, the polarization product P_iP_j was calculated from the following relation:

$$P_i(E_i, \theta_i)P_j(E_j, \theta_j) = \frac{R-1}{R+1}, \quad (1)$$

where P_i and P_j are the polarizations produced in the unpolarized beam scattering at energies and angles E_i, θ_i , and E_j, θ_j , in the center of mass system, respectively. The sign convention for the polarization was that the positive direction is that of $\mathbf{k}_{ino} \times \mathbf{k}_{so}$, where $\mathbf{k}_{ino}$ and $\mathbf{k}_{so}$ are the incident and scattered wave vectors, respectively.

We made three interdependent measurements in which the polarization product P_iP_j was equal to P_1P_2 , P_2P_3 , or P_3P_1 , as has been done by Scott⁴⁾. The results of these measurements can be analysed in terms of three equations in three unknowns. The absolute

* Institute for Nuclear Study, University of Tokyo.

** Department of Physics, Faculty of Science, Kyoto University.

*** Department of Applied Science, Faculty of Technology, University of Hiroshima.

**** Department of Nuclear Engineering, Faculty of Engineering, Kyushu University.

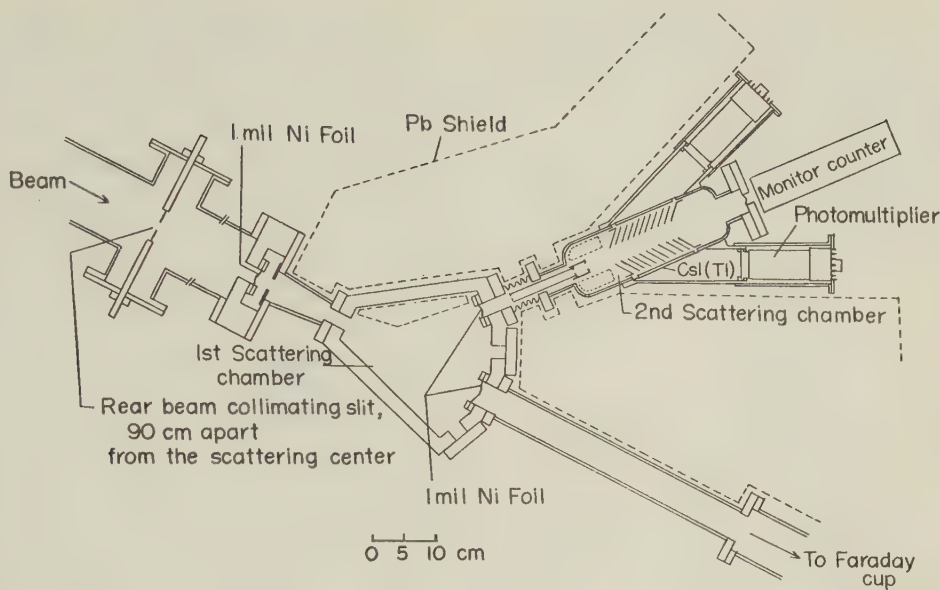


Fig. 1. Double scattering chamber. Front beam collimating slit is not shown. The distance between front and rear beam collimating slits was 121 cm.

Table I. Experimental conditions.

	Target	Scattering angle	Distance between scattering centers	Detector	Particles and their energy***
$-P_1^*$	H ₂ 5 atm. or Polyethylene foil 8.35 mg/cm ²	25.0° ± 1.6°****	648.5 mm	CsI(Tl) and RCA 6342	Alpha-particles 30.7 ± 0.3 MeV
P_2^{**}	He 4 atm.	50.0° + 10.5° - 8.1°			Protons 14.4 ± 0.2 MeV
P_2^*	He 2.8 atm.	50.0° ± 2.7°	348.5 mm	CsI(Tl) and RCA 6342	Protons 14.4 ± 0.1 MeV
P_3^{**}	He 2.8 atm.	50.0° + 10.5° - 8.1°			Protons 11.4 ± 0.1 MeV
P_3^*	He 4.9 atm.	50.0° ± 2.7°	365.0 mm	Ilford C-2 100 μ Plates	Protons 11.4 ± 0.1 MeV
P_1^{**}	He 4.9 atm.	117.0° + 10.8° - 13.3°			Protons 7.9 ± 0.2 MeV

* Polarization produced in the first scattering, when the unpolarized beam is used.
** Polarization produced in the second scattering, when the unpolarized beam is used.
*** Energy in the laboratory system at the scattering center.

value of the individual polarization may then be calculated from the following relations:

$$\left. \begin{aligned} |P_1| &= (|P_1P_2| \cdot |P_3P_1| / |P_2P_3|)^{1/2}, \\ |P_2| &= (|P_1P_2| \cdot |P_2P_3| / |P_3P_1|)^{1/2}, \\ |P_3| &= (|P_2P_3| \cdot |P_3P_1| / |P_1P_2|)^{1/2}. \end{aligned} \right\} \quad (2)$$

Two sets of signs of the individual polarization are available from Eq. (1) and Eq. (2). But, if the sign of a polarization is known,

then the signs of another two polarizations can be determined from Eq. (1).

§ 3. Procedures

Our variable energy cyclotron is available for the beams of 7.5~15 MeV protons and 30~42 MeV alpha-particles. Using both of alpha-hydrogen and proton-helium scattering, we selected the energies and angles, in the

center of mass system, of three polarizations, which are $P_1(6.2 \text{ MeV}, 130.0^\circ)$, $P_2(11.5 \text{ MeV}, 61.1^\circ)$ and $P_3(9.1 \text{ MeV}, 61.1^\circ)$. The experimental conditions in the laboratory system are summarized in Table I.

The second scattering chamber is an analyzer of the polarization produced in the first scattering. Its details are shown in Fig. 2.

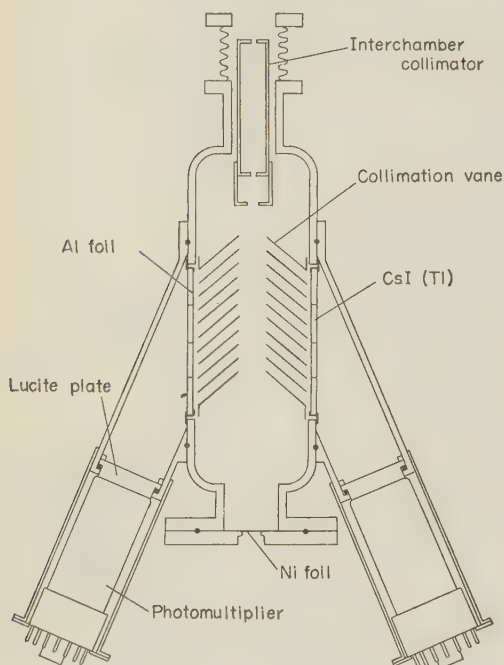


Fig. 2. Analyzer.

Collimation vanes set at an angle of 50° or 117° defined the scattering angle, the target thickness and the solid angle. The scintillation crystals were thallium-activated cesium iodide of $2 \text{ cm} \times 10 \text{ cm}$ and 0.15 cm thick, which was composed of four sheets in a row. Such a geometry increased the counting rate, as pointed out by Sorokin and Taranov, and by Brockman⁷⁾. However, it resulted in a poor resolution of the pulse height spectrum, about 50 percent. Before setting up the analyzer, we investigated the character of the detectors by moving the collimated polonium alpha source along the surface of scintillation crystals. We found that the main cause of the poor resolution is the difference in pulse heights, which originate from the scintillations produced at different positions in the crystal.

The gas pressure of the order of 5 atmospheres was sustained by Lucite plates, which

were in contact with the photomultiplier tubes. The special regard was paid to keep away the hydrogenous substances from the scintillation crystals in order to reduce the background produced by neutrons. In spite of such a consideration and shieldings at the outside of the chamber, the background due to gamma rays and neutrons was too much to separate the lower side of the pulse height spectrum of scattered protons from the rise of background pulses, in the early stage of the experiment. Then, we searched the sources of background radiations. They were 1-mil nickel foils traversed by the incident beam, which were placed at the entrance and the exit of the first scattering chamber. By lengthening the interchamber pipe and inserting shielding blocks in the inside of the chamber, the improvement was achieved. More improvement was resulted, when we removed the exit nickel foil and filled the pipe after the first chamber with gas. The incident beam lost almost of its energy in the gas before hitting an another foil. In the case of alpha-hydrogen scattering, the polyethylene foil was used successfully as the target in the first chamber.

Examples of the pulse height spectrum are shown in Figs. 3 and 4. Fig. 3 shows the pulse height spectrum of protons, which entered the second chamber from the first chamber. It was detected by a CsI(Tl) scintil-

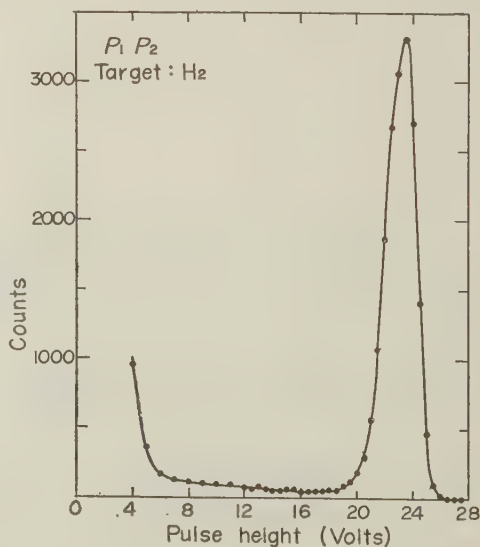


Fig. 3. Pulse height spectrum of recoil protons in the measurement of $P_1 P_2$, which entered the second chamber from the first chamber.

lator, after passing through the second chamber. Its full width at half maximum was 5 percent. Fig. 4 shows the pulse height spectrum of doubly scattered protons. The background spectrum is also shown. The background spectrum was taken by evacuating the second chamber or covering scintillation crystals with shutters thick enough to stop scattered protons.

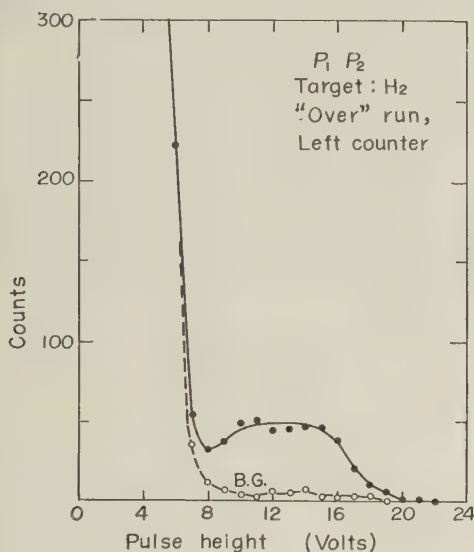


Fig. 4. Pulse height spectrum of doubly scattered protons in the measurement of P_1P_2 . Pulse height spectrum of background is also shown.

In the measurement of P_3P_1 , we tried at first to detect doubly scattered protons with thinner CsI(Tl) crystals, 0.03 cm thick, to suppress the background. But we could not separate the proton spectrum from the background. Then, we used Ilford C-2 100 micron plates of 1 inch $\times$ 3 inch, which were placed immediately after the collimation vanes with a glancing angle of 20° . Two plates were used one upon another on each side. The under plates recorded only the tracks of protons knocked out by background neutrons.

The scanned area was $3.8\text{ cm} \times 1.5\text{ cm}$ of each plate. The criteria adopted were that the track must (a) enter the surface of the emulsion, (b) have an azimuthal angle within the limit defined by collimation vanes and (c) not dip into the unshrunk emulsion at an angle greater than 31° . Especially, the care was taken about the direction of the particle, the change of ionization density along the

track. The background plates were scanned with the same criteria. Fig. 5 shows an example of the range spectrum on an upper plate. The range of the peak corresponds well to the mean energy of doubly scattered protons and the width is explained by the energy variation due to the spread of the scattering angle.

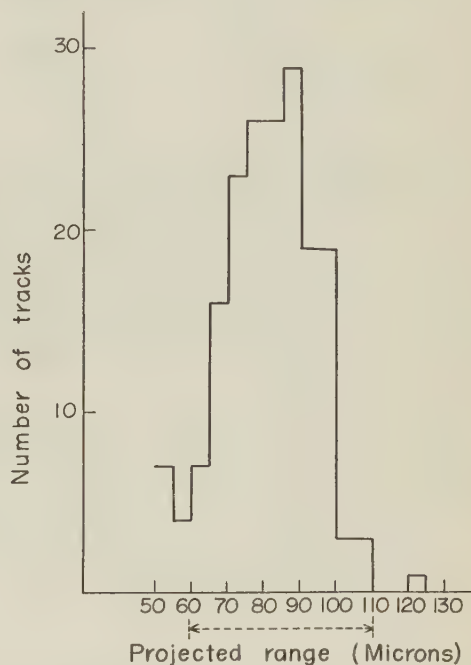


Fig. 5. Projected range spectrum of the tracks in an upper plate in the measurement of P_3P_1 .

Though the geometry in the second chamber including the interchamber collimator was set with great care, misalignment might be still remained. Moreover, the right and left detector systems were not strictly equal. All these caused the asymmetry due to instrumentation. We repeated all runs with the second chamber rotated through 180° about its own axis and averaged the results of the up and over runs to cancel the above-mentioned asymmetry.

§ 4. Results and Discussions

The results of the polarization products are indicated in Table II. The left-right ratios are also shown. The estimated errors are due to the counting statistics and the background subtraction. Corrections described in the following have already been applied to the left-right ratios.

Table II. Left-right ratios and polarization products.

		<i>R</i>	Average <i>R</i>	Polarization product
$-P_1P_2$	up	2.14 ± 0.20	2.40 ± 0.18	0.41 ± 0.03
	over	2.70 ± 0.22		
P_2P_3	up	1.74 ± 0.25	1.51 ± 0.14	0.20 ± 0.04
	over	1.31 ± 0.17		
P_3P_1	up	0.42 ± 0.06	0.42 ± 0.05	-0.41 ± 0.04
	over	0.42 ± 0.06		

The scattering cross section in the first scattering falls off with increasing angle. This causes the nonuniform illumination of helium in the second scattering by protons from the first chamber. The correction for the left-right ratio due to this effect was calculated. The results were 0.7 percent in the case of P_1P_2 and 0.2 percent, negligible, in the other two cases.

Further, we must consider the fact that the scattering cross section and the polarization change with angle, because the spread of the scattering angle in the second scattering was large. The measured left or right intensity was proportional to the quantity

$$\int \sigma(\theta) \{1 \pm P_i P_j(\theta)\} G(\theta) d\theta,$$

where $G(\theta)$ is the geometrical factor determined from the geometry of collimation vanes. We calculated the correction for the left-right ratio, in order to normalize to the value obtained if $P_j(\theta)$ is constant and equals to the one for the mean scattering angle. The values of cross sections and polarizations in the necessary angular range were estimated from phase shifts obtained so far^{(8), (9)}. Fig. 6 shows the calculated angular distribution of the polarization. Above 10 MeV, the values of phase shifts have not yet been determined completely, especially being obscure about D -wave phase shifts. Then, we used only S - and P -wave phase shifts above 10 MeV. Corrections amounted to 3.9 percent in the measurement of P_3P_1 , 0.5 percent in that of P_1P_2 and negligible, the order of magnitude of 0.1 percent, in that of P_2P_3 .

Using the values of the polarization products shown in Table II, the individual polarizations were calculated. The results are:

$$P_1(6.2 \text{ MeV}, 130.0^\circ) = 0.92 \pm 0.11$$

$$P_2(11.5 \text{ MeV}, 61.0^\circ) = -0.45 \pm 0.06$$

$$P_3(9.1 \text{ MeV}, 61.1^\circ) = -0.45 \pm 0.06,$$

where angles and energies are those in the center of mass system. In Fig. 6, these experimental values in the laboratory system are also shown. The agreement with the calculated values is satisfactory. Both of differential cross sections and polarizations were fitted, even up to 15 MeV, with phase shifts which imply the inverted doublet for the ground and first excited state of Li^2 .

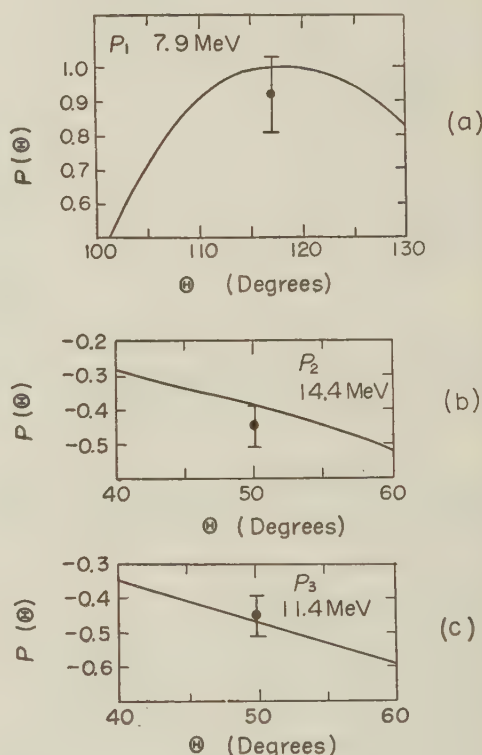


Fig. 6. Calculated angular distribution of the polarization. Angles and energies are those in the laboratory system. Phase shifts used in the calculation are:

- (a) $\delta_0 = -59^\circ 26'$, $\delta_1^- = 52^\circ 32'$, $\delta_1^+ = 111^\circ 30'$,
 $\delta_2^- = -2^\circ 38'$, $\delta_2^+ = -17'$,
- (b) $\delta_0 = -78^\circ 42'$, $\delta_1^- = 49^\circ 54'$, $\delta_1^+ = 92^\circ 12'$,
- (c) $\delta_0 = -70^\circ 0'$, $\delta_1^- = 52^\circ 48'$, $\delta_1^+ = 102^\circ 18'$.

The values of the polarization calculated by Brockman⁽⁷⁾, and by Gammel and Thaler⁽¹⁰⁾ agree with the results of the present work within the experimental error. Those calculated by Lasinio and Monetti⁽¹¹⁾, and by Bradner and Isbell⁽¹²⁾ differ slightly from the present experimental values.

Acknowledgement

The authors wish to express their appreciations to Professors S. Kikuchi and I. Nonaka for the constant encouragement. They are grateful to Prof. S. Yamabe and his colleague of Osaka University for the joint efforts to make the double scattering chamber, and also to operating crew of the cyclotron, particularly Messrs. T. Karasawa, A. Suzuki and H. Ogawa.

References

- 1) The scattering of nucleons by helium was reviewed by P. H. Hodgson: *Advances in Physics*, **7** (1958) 1.
- 2) C. L. Critchfield and D. C. Dodder: *Phys. Rev.* **76** (1949) 602. L. Wolfenstein: *Phys. Rev.* **75** (1949) 1664. J. V. Lepore: *Phys. Rev.* **79** (1950) 137. L. Puzikow, R. Ryndin and J. Smorodinsky: *Nucl. Phys.* **3** (1957) 436.
- 3) M. Heusinkveld and G. Freier: *Phys. Rev.* **85** (1952) 80.
- 4) M. J. Scott: *Phys. Rev.* **110** (1958) 1398.
- 5) A. C. Juveland and W. K. Jentschke: *Z. Physik* **144** (1956) 521.
- 6) L. Rosen and J. E. Brolley, Jr.: *Phys. Rev.* **107** (1957) 1454.
- 7) P. V. Sorokin and A. Ia. Taranov: *Soviet Phys. Dokl.* **1** (1956) 637. K. W. Brockman, Jr.: *Phys. Rev.* **108** (1957) 1000; **110** (1958) 163.
- 8) J. Sanada: *Proc. Phys. Soc. Japan* **14** (1959) 1463.
- 9) T. M. Putnum, J. E. Brolley, Jr. and L. Rosen: *Phys. Rev.* **104** (1956) 1303. P. D. Miller and G. C. Phillips: *Phys. Rev.* **112** (1958) 2043.
- 10) J. L. Gammel and R. M. Thaler: *Phys. Rev.* **109** (1958) 2041.
- 11) G. J. Lasinio and G. C. Monetti: *Nuovo Cimento* **6** (1957) 989.
- 12) H. Bradner and W. Isbell: *Phys. Rev.* **108** (1957) 463.

Elastic and Inelastic Scattering of Protons from N, Ne, Mg, Si, S and A in the Energy Range from 7.6 MeV to 14.2 MeV

By Yukiyasu ODA*, Minoru TAKEDA**, Naoyuki TAKANO***,
Takashi YAMAZAKI**, Chuin HU**,
Ken KIKUCHI****, Shinsaku KOBAYASHI*****,
Kazuhisa MATSUDA***** and Yukio NAGAHARA*****

Institute for Nuclear Study, University of Tokyo, Tanashi-machi, Tokyo

(Received January 9, 1960)

The angular distributions of protons scattered elastically and inelastically by N, Ne, Mg, Si, S and A nuclei have been studied at several values of proton energy from 7.6 to 14.2 MeV. The distribution shapes for elastic scattering show generally diffraction patterns at $E_p > 10$ MeV. While the yields of inelastic scattering corresponding to the second excited state of N^{14} are appreciable at higher energies, the yields for the first excited state with $T=1$ are markedly low. The inelastic scatterings for the first excited states of Ne^{20} , Mg^{24} and Si^{28} are found to change their distribution shapes appreciably with proton energy. The excitation functions of the reaction for Si^{28} were also studied. The results show prominent resonance features. These results seem to support that the formation of compound nucleus plays an appreciable role in the inelastic scattering from these light nuclei, especially at the lower energy. The distribution shapes of the inelastic scattering from S^{32} are fairly insensitive to energy change. Further, the inelastic scattering of protons from A^{40} shows quite a different feature from those mentioned above. The angular distribution shapes and their energy dependences resemble much those obtained for medium weight even-even nuclei.

§ 1. Introduction

In this paper the experimental studies for the scattering of medium energy protons from light nuclei are described. Protons of energies from 7.6 MeV to 14.2 MeV were produced by the I.N.S. (Tokyo) Cyclotron. The target elements studied were nitrogen, neon, magnesium, silicon, sulphur and argon.

Some of the present authors (Osaka group) studied the scatterings of protons by these nuclei in the lower energy region near 5

MeV¹⁻⁴⁾. They found many resonance features in the inelastic scattering for these nuclei and also some rapid changes with energy in the elastic scattering angular distributions. It was also shown that both the angular distribution shapes and the absolute values of the cross sections are able to be interpreted on the basis of the compound nucleus theory²⁾⁻⁴⁾.

Some of the present authors (I.N.S. group) studied the scatterings of protons by medium weight even-even nuclei; Ti, Cr, Fe and Ni⁵⁾, at 14.1 MeV. They found for all these nuclei the elastic scattering angular distributions of diffraction pattern type and the inelastic scattering angular distributions expected from the direct process theory. These features have been confirmed recently in another experiment carried out by all of the present authors⁶⁾. Thus it was the purpose of the present work to find what kind of feature is observed for the elastic and inelastic scat-

* Department of Physics, Osaka University, Osaka. Now at Physics Department, Tokyo Institute of Technology, Meguro-ku, Tokyo.

** Department of Physics, Osaka University, Osaka.

*** Department of Physics, Kyushu University, Fukuoka.

**** Institute for Nuclear Study, Tokyo. Now at Minnesota University.

***** Institute for Nuclear Study, Tokyo.

***** Department of Physics, Yokohama National University, Yokohama.

tering of protons by light nuclei in the same energy region. For this purpose a study of the angular distributions for nuclei mentioned above was carried out by changing the energies of incident protons from 7.6 MeV to 14.2 MeV.

§ 2. Apparatus

The energy of the proton beam was varied by adjusting the cyclotron and the focusing magnet. Details of the apparatus, especially of scattering chamber, beam collector, scintillation detectors and electronics were nearly the same as that described in the previous papers^{5), 6)} and are not repeated here.

Gas targets were employed for nitrogen, neon, sulphur (H_2S) and argon. They were filled in a gas container which was made from a brass cylinder of 90 mm in diameter and had a window of wide angular opening covered with aluminium foil of $20\ \mu$ in thickness. The magnesium target of $2.0\ \text{mg}/\text{cm}^2$ in thickness was prepared by evaporation. A thin fused silica foil of $1.62\ \text{mg}/\text{cm}^2$ was used for silicon experiment. In the cases of gas target, a pair of slits of rectangular shape was placed just before the detector on the turn table. They define the effective thickness of the targets in an usual manner.

§ 3. Experimental Procedures

The energies of the proton beam were measured by the absorption method described in our previous paper⁵⁾. The accuracy seems to be about 1.0% in absolute value*. On the other hand, the energy spread of the incident beam would be about of same order.

As the first excited states of nuclei of the most abundant isotopes of our target element are situated fairly apart from the ground states, the inelastic scattering groups corresponding to these excited states are well distinguished in the pulse height spectrum. Some typical examples are shown in Figs. 1(a) to 1(h) for various conditions. As is seen in these figures, the proton groups corresponding to the higher excited states were also observed simultaneously.

The cyclotron was operated as continuously

as possible for some ten hours a run. A series of sets of measurements for the angular distributions were performed for six targets mentioned already at several values of proton energy. The absolute values of these incident energies were measured in every case. The scattering angles studied ranged from 20° to 165° in laboratory system with a step of 5° or 7.5° .

Excitation functions for the reaction $\text{Si}^{28}(p, p')\text{Si}^{28*}$ ($Q = -1.78\ \text{MeV}$) at the laboratory

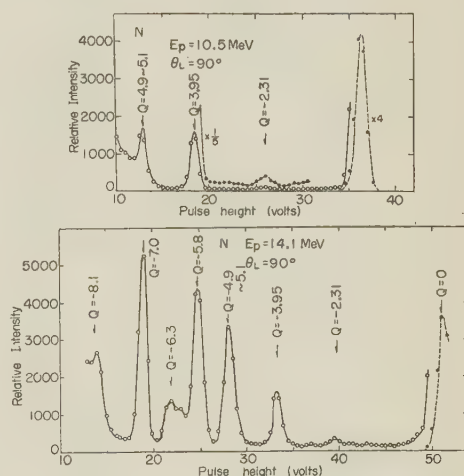


Fig. 1(a)(b). Proton spectra from $\text{N}^{14}(p, p')\text{N}^{14*}$.

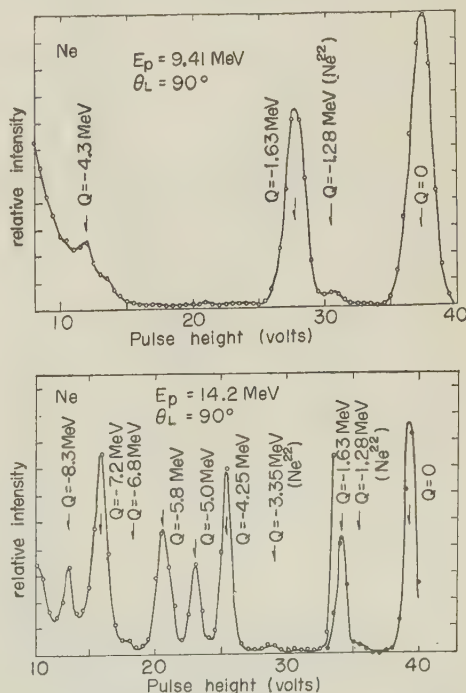


Fig. 1(c)(d). Proton spectra from $\text{Ne}(p, p')\text{Ne}^*$.

* In the case of H_2S , the energies of the proton beam were not measured, but were determined by the cyclotron parameters. Therefore the accuracy seems to be a little worse in absolute value.

angles of 45° and 90° were observed with 50 keV step in the ranges from 8.30 MeV to 9.25 MeV and from 11.4 MeV to 12.1 MeV respectively.

The accuracies of the differential cross sections obtained in these measurements would

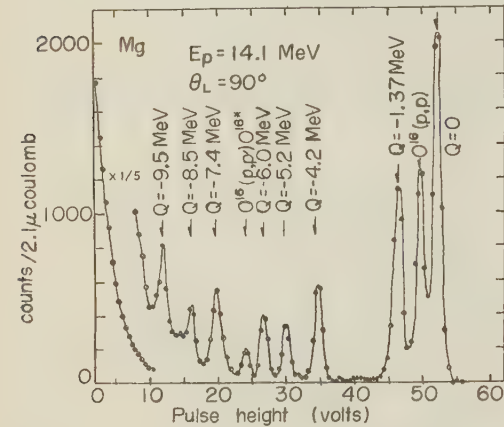


Fig. 1(e). Proton spectrum from Mg(p, p')Mg*.

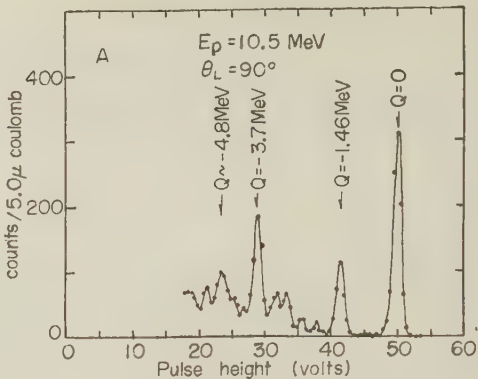


Fig. 1(h). Proton spectrum from A(p, p')A*.

be about 5% in relative values except at small angles. The accuracy of the absolute value may be good for the gas targets (within 5%) except at the lowest proton energies, and not so good for the foils targets (within 20%).

§ 4. Results

The results for the angular distributions of the elastic scattering from the nuclei above mentioned except silicon are shown in Fig. 2 to Fig. 6. Owing to the presence of oxygen in the SiO₂ target, the angular distributions of the elastic scattering from silicon are not included here.

It is recognized that at higher proton energies the angular distributions show diffraction patterns as in the cases of medium weight

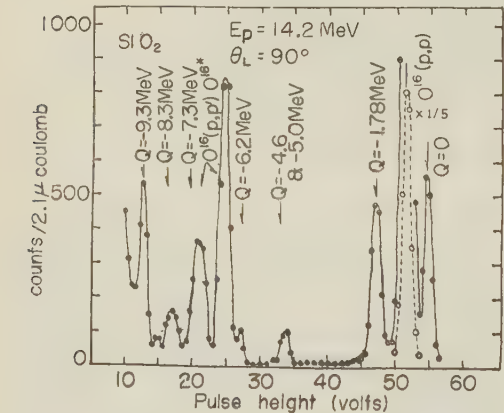


Fig. 1(f). Proton spectrum from SiO₂(p, p').

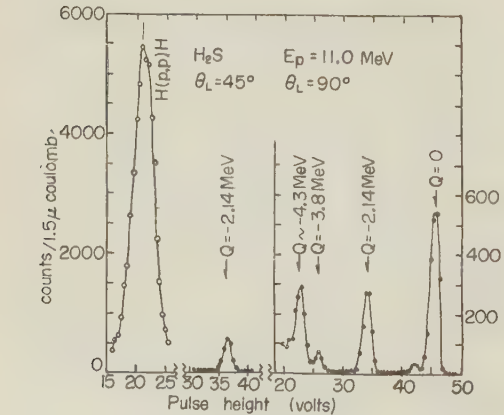


Fig. 1(g). Proton spectrum from S(p, p')S*.

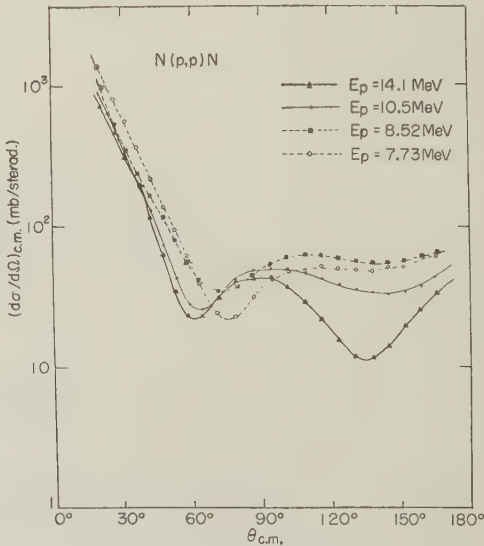


Fig. 2. Angular distributions of elastic scattering on Nitrogen.

elements⁶⁾. At lower energies, however, the diffraction features are not so evident.

The results for the angular distributions of the inelastic scattering corresponding to the first and second excited states of N^{14} and of that corresponding to the first excited states of Ne^{20} , Mg^{24} , Si^{28} , S^{32} and A^{40} are shown in

Fig. 7 to Fig. 13. In Fig. 14 the total cross sections of these reactions are plotted against the incident energy. Some results given in the published articles which will be cited later are also included in Fig. 14 for comparison.

While the proton group of the reaction $N^{14}(p, p')N^{14*}$ with $Q = -2.31$ MeV was ob-

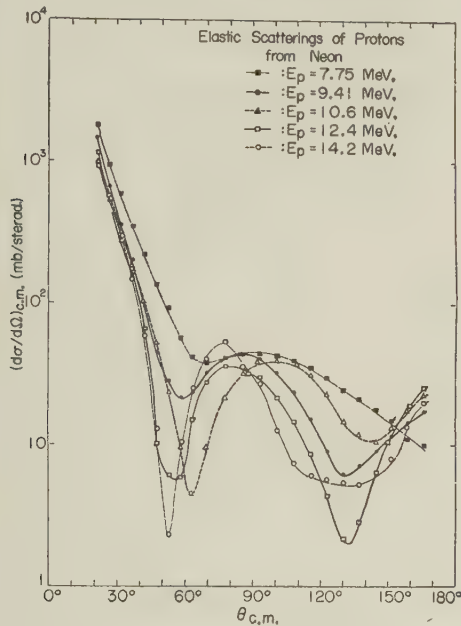


Fig. 3. Angular distributions of elastic scattering on Neon.

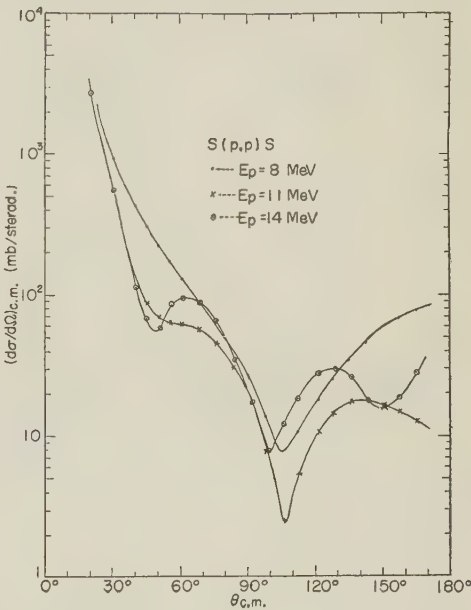


Fig. 5. Angular distributions of elastic scattering on Sulphur.

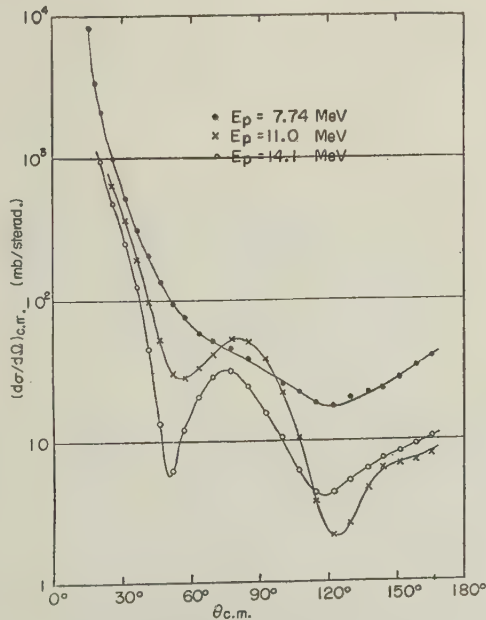


Fig. 4. Angular distributions of elastic scattering on Magnesium.

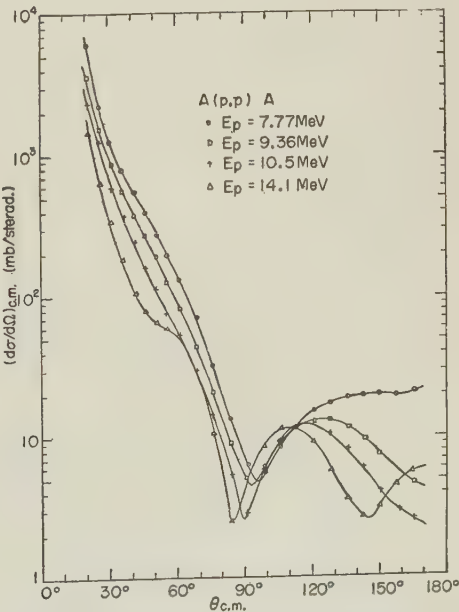


Fig. 6. Angular distributions of elastic scattering on Argon.

served in the whole region of proton energies it was hard to detect the group of the reaction with $Q = -3.95$ MeV in the lower energy region due to the large gamma-ray background. In the region of the higher proton energies, however, the intensity of the 2.31 MeV group became very weak. These features are shown partly in Fig. 1(a) and (b).

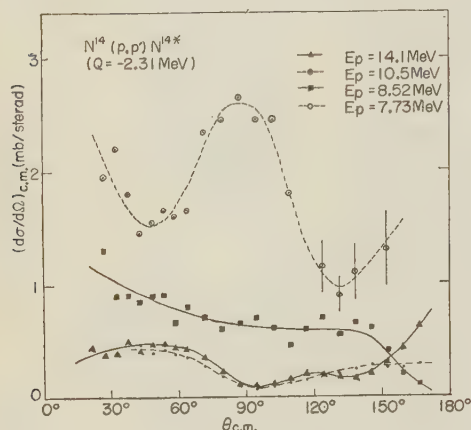


Fig. 7. Angular distributions of inelastic scattering (1st excited state) on Nitrogen.

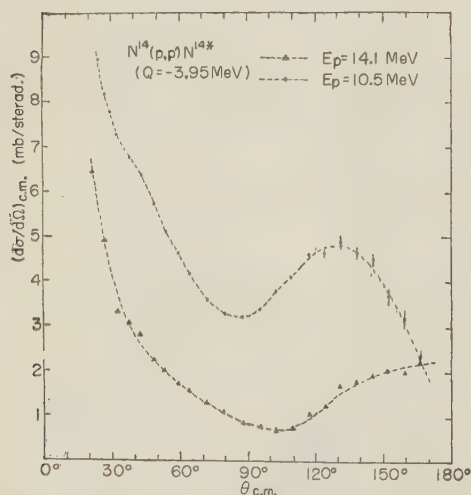


Fig. 8. Angular distributions of inelastic scattering (2nd excited state) on Nitrogen.

As is seen in Fig. 9, the angular distributions of the reaction $\text{Ne}^{20}(p, p')\text{Ne}^{20*}$ ($Q = -1.63$ MeV) change their shapes remarkably with the energy of incident protons†. The

result at $E_p = 9.5$ MeV resembles that by Freeman et al.⁷⁾ except the features in backward scattering.

Our results for the inelastic scatterings to the first excited state of Mg^{24} are shown in Fig. 10†. Distribution shapes are somewhat different from those obtained previously by other authors^{8)–11)} but the absolute values seem to be consistent with them.

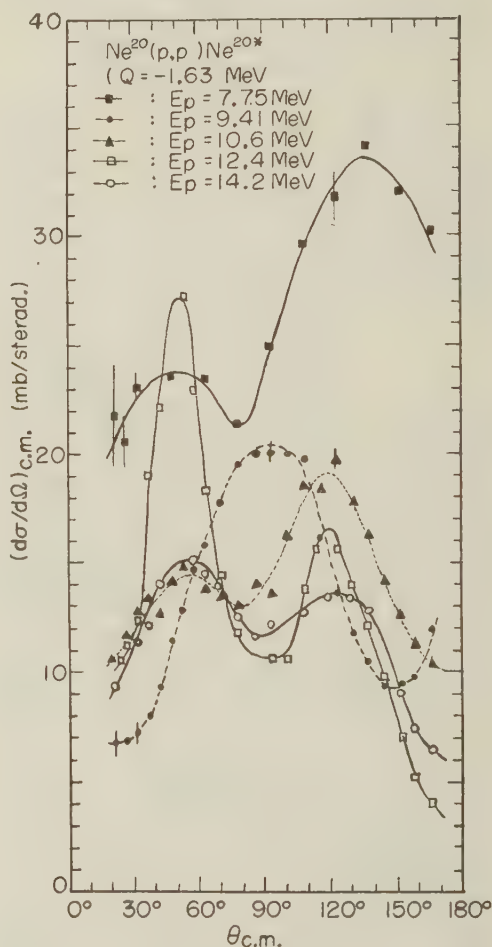


Fig. 9. Angular distributions of inelastic scattering (1st excited state) on Neon.

As is seen in Fig. 11, the angular distributions of the reaction $\text{Si}^{28}(p, p)\text{Si}^{28}$ ($Q = -1.78$ MeV) change also rapidly with proton energy. This feature was pointed out previously by Greenless et al.¹²⁾ in the energy region from 7.97 to 9.45 MeV. The variations found in our results are, however, more prominent than that in their work. Further, our result of the angular distribution at 7.64 MeV does not resemble those obtained by them at nei-

† Further investigations for the elastic and the inelastic scattering from Ne and Mg together with those from C and O have been done recently by some of us. The results will be published in the near future.

bouring energies. As the energy equivalence of our target thickness is about 80 keV in this energy region, some energy dependent features appeared if they are existent.

Similar disagreements with the published data are found in the high energy region investigated in this work. Conzett studied the angular distribution of the present reaction at 12 MeV¹¹. His result, however, resembles neither of our results at 11.3 nor at 14.2 MeV. The changes of the angular distribution with energy are thus expected.

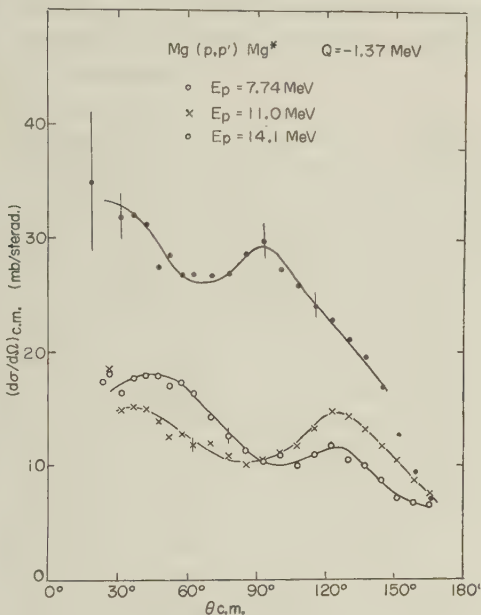


Fig. 10. Angular distributions of inelastic scattering (1st excited state) on Magnesium.

The angular distributions for the reactions $S^{32}(p,p')S^{32*}$ ($Q=-2.24$ MeV) are shown in Fig. 12. It is worth while to note that the absolute values of the differential cross sections for the P-P scatterings due to hydrogen contained in the gas target are found to agree well with the experimental values published in literature. Fig. 1(g) show the relative intensities of this group and other group due to the scattering from sulphur. The angular distributions change their shapes with proton energies. It must be further pointed out in Fig. 14 that the reaction cross sections seem to be smaller than those obtained for the lighter nuclei at nearly the same energies.

The results for the reaction $A^{40}(p,p')A^{40*}$ ($Q=-1.46$ MeV) are shown in Fig. 13. The

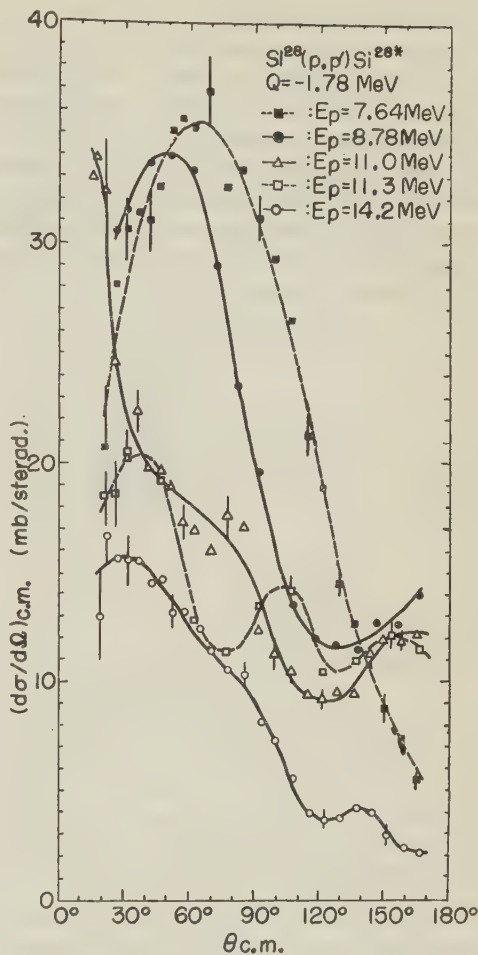


Fig. 11. Angular distributions of inelastic scattering (1st excited state) on Silicon.

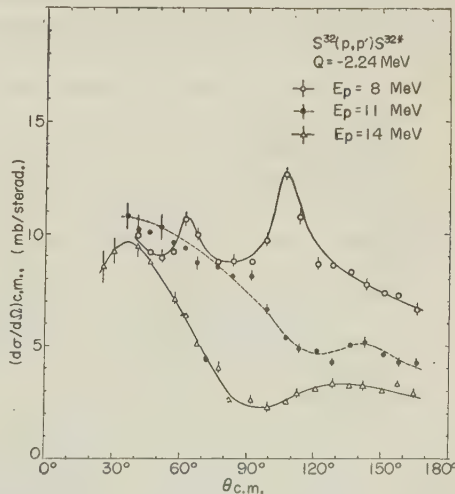


Fig. 12. Angular distributions of inelastic scattering (1st excited state) on Sulphur.

feature mentioned above in the case of sulphur concerning the absolute values of the reaction cross sections seems to be more evidently in this case. And the variation of the angular distributions seems to be moderate compared with the case of the lighter nuclei. Similar distribution shapes and cross section values were obtained previously by Eisberg and Hintz¹³⁾ at the proton energies of 8.5, 9.0 and 9.8 MeV.

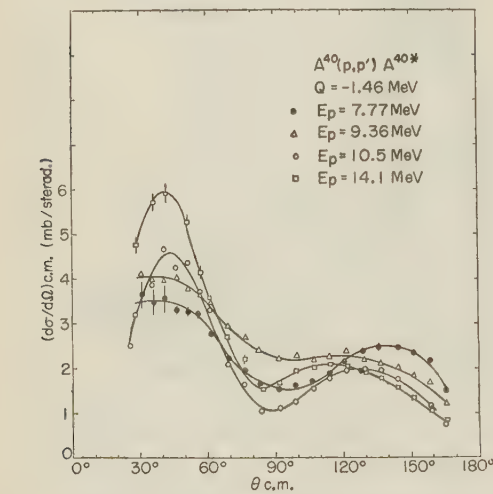


Fig. 13. Angular distributions of inelastic scattering (1st excited state) on Argon.

Although the distribution shape studied by Freemantle et al.⁷⁾ at 9.51 MeV is somewhat different from that obtained by the present authors at 9.36 MeV and from that by Eisberg and Hintz at 9.8 MeV, the differences among them are confined to the region of small scattering angles. The study of this reaction

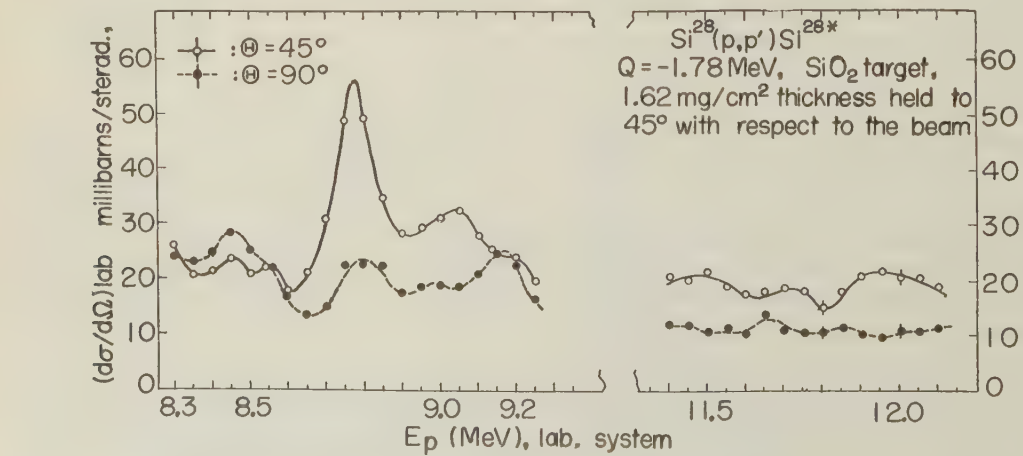


Fig. 15. Excitation curve of inelastic scattering (1st excited state) on Silicon.

at the lower energy of 5.5 MeV made by Osaka Group¹⁴⁾ revealed further an angular distribution which is similar to those obtained in this experiment at 7.77 and 9.36 MeV. From these data we may conclude that the inelastic scatterings of protons $A^{40}(p, p')A^{40*}$ ($Q = -1.46 \text{ MeV}$) have smaller cross sections than those for the first excited states of the lighter even-even nuclei, and the change of the distribution shapes with proton energy is less remarkable.

In order to confirm the rapid changes of the inelastic scattering with proton energies found in the case of Ne^{20} , Mg^{24} and Si^{28} , we studied the excitation function of the reaction

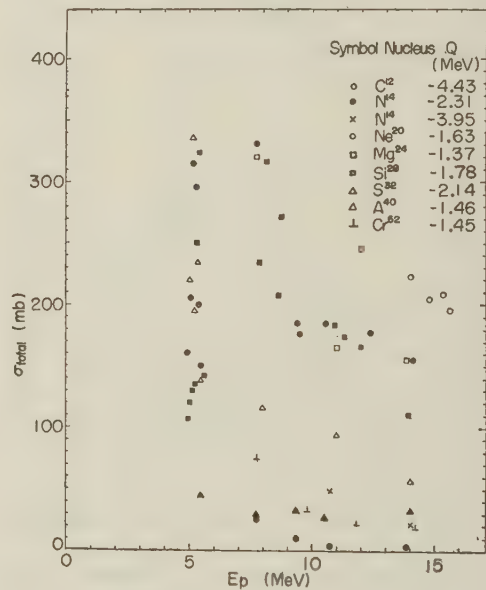


Fig. 14. The total cross sections of (p, p') reactions.

$\text{Si}^{29}(p, p')\text{Si}^{28*}$ ($Q = -1.78$ MeV) at the laboratory scattering angles of 45° and 90° in the regions of energies from 8.3 to 9.25 MeV and from 11.4 to 12.1 MeV with an energy step of 50 keV. The results are shown in Fig. 15. As can be seen evidently from these curves, the energy dependence of the reaction is remarkable at the lower energy region but fairly smooth at the higher energy region. We found a prominent anomaly at 8.78 MeV with a half width of about 100 keV. The differential cross sections $\sigma(45^\circ)$ and $\sigma(90^\circ)$ at 12.0 MeV are found to be consistent with that obtained by Conzett¹¹⁾.

§ 5. Discussion

A. Elastic scattering

Generally speaking, the angular distributions of elastic scattering shown in Fig. 2 to Fig. 6 show the so-called diffraction patterns especially in the higher energy region. The distribution shape for argon at 14.1 MeV resembles well that for titanium at the same energy in our previous paper⁶⁾, which reports the results for medium weight nuclei. However, the variations of differential cross sections of neon with energy near 10.6 MeV make one expect the probable existence of an anomaly. In the lower energy region, the angular distribution shapes obtained in this work do not show so marked diffraction pattern as in the higher energy region. Also, we cannot find such a simple proportionality of the angle of the first scattering minimum $\theta_{\min}$ to $A^{-1/3}$ as has been seen in the case of medium weight nuclei above 10 MeV⁶⁾.

B. Inelastic scattering

The angular distributions of inelastic scattering studied in this work show variant features depending probably on the natures of the target nuclei.

$\text{N}^{14}(p, p')\text{N}^{14*}$, $Q = -2.31$ and -3.95 MeV

Bair et al.¹⁵⁾ observed the resonance inelastic scattering to the first excited state of nitrogen ($Q = -2.31$ MeV) in the energy range of $E_p \leq 5$ MeV, but the Osaka group¹⁶⁾ did not observe the yield of this reaction at $E_p = 5.6$ MeV. Bockelman et al.¹⁷⁾ found that the yield of this process is 5% of that for the elastic scattering and is about one half of that for the inelastic scattering to the second excited state ($Q = -3.95$ MeV) at $E_p = 6.98$ MeV, $\theta_{\text{lab}} = 90^\circ$. This fact was discussed by them in

comparison with the inelastic scattering of deuterons, where the yield to the first excited state is less than 0.5% of that to the elastic scattering at the same incident energy and at the same angle (isotopic spin selection rule). Freemantle et al.⁷⁾ showed, however, that the yield for the first excited state was less than 1/6 of that for the second excited state at $E_p = 9.51$ MeV. They also showed that the angular distribution of the inelastic scattering to the second state was nearly symmetric about 90° .

Table I. The total cross sections of the inelastic scattering from nitrogen (mb).

E_p (MeV)	Q (MeV)	
	-2.31	-3.95
7.73	24.0	—
8.52	8.0	—
10.5	3.2	57.8
14.1	3.4	22.5

Our results are shown in Table I, which confirm the fact that the yields to the first excited state are very small over the wide range of the incident energy, in comparison with those to the higher excited states and with those to the first excited states of the other even-even nuclei studied in this work. The small yield of this reaction lead us to some consideration about the reaction mechanism. Owing to the odd-odd character of this nucleus, the (p, n) channel opens at the lower energy ($Q = -5.93$ MeV) than the neighbouring even-even nuclei. So we are likely to attribute the small yields to this character of the target nucleus. As shown in Fig. 1, however, the yields of some groups to the higher excited states are not so small. If the direct process is assumed, for the reaction, this fact might be caused by the difference between the natures of the ground state and of the first excited state or by the reason which was suggested by Levinson and Barnergee¹⁸⁾. Sano, suggested us that the non-flipping nature of the spin angular momentum may lead to such a forbidden transition.

Inelastic Scattering from even-even Nuclei.

The spins and parities of the ground states of nuclei, Ne^{20} , Mg^{24} , Si^{28} , S^{32} and A^{40} are all $0(+)$, and those of the first excited states of these nuclei which are relevant to the present

results are all $2(+)^{19}$. Our results for the angular distributions of protons in the $0(+)\rightarrow 2(+)$ transitions which have been obtained for the medium weight nuclei in the same energy region have revealed the distribution patterns expected by the direct process theory⁶⁾⁻⁷⁾. As is shown in the following, the present results for above light even-even nuclei show variant features characteristic to each nucleus.

$\text{Ne}^{20}(p, p')\text{Ne}^{20*}$, $Q = -1.63$ MeV

Butler showed that the angular distribution of this reaction obtained by Freemantle et al. at 9.51 MeV⁷⁾ can be reproduced by the direct process theory employing the Born approximation²⁰⁾. At lower energies, Osaka group obtained very similar distribution patterns accompanying with resonance phenomena¹⁾.²⁾ Our present results of this reactions show the marked energy dependency of the distribution shapes. The distribution shapes obtained at 7.75 and 10.6 MeV are quite different from that at 9.41 MeV which is similar to the result by Freemantle et al. This feature can not be understood easily on the basis of the simple direct theory, because the results of this theory are usually expected not to be so sensitive to the energy change²⁰⁾.

Thus the reaction in this energy region seems to proceed appreciably through an energy dependent process such as compound nucleus formation. As is seen in Fig. 14, the large total cross section of 330 mb at 7.75 MeV makes one expect an anomaly near this energy, because Osaka group have obtained that the total cross section at 5.25 MeV resonance is 320 mb and the off-resonance cross section at 5.50 MeV is 150 mb²⁾.

Contrary to the low values of the cross sections found in the case of $\text{N}^{14}(p, p')\text{N}^{14*}$, the total cross sections obtained for neon are generally quite large. The magnitudes are of the same order as those of the total cross sections of the reaction $\text{C}^{12}(p, p')\text{C}^{12*}(Q = -4.43$ MeV) studied by Conzett¹¹⁾ and Peelle²¹⁾, which are 246 to 200 mb in the region of $E_p = 12.0$ to 15 MeV.

It is seen in Fig. 14 that the total cross section of this reaction decreases gradually with increasing proton energy near 13~14 MeV, and reduces to 156 mb at $E_p = 14$ MeV. This reduction of the total cross section is related, however, to the increase of the yields

of other reactions corresponding to the higher excited states of the target nucleus.

As shown in Fig. 1(d) for $E_p = 14.2$ MeV, those groups of the inelastically scattered protons which leave the nuclei in the higher excited states are well observed. We could study unambiguously the angular distributions of the groups corresponding up to the fourth excited state[†]. The total cross sections thus obtained are 49.9 mb, 20.6 mb and 62.0 mb for the second ($Q = -4.25$ MeV), third ($Q = -5.2$ MeV), and fourth ($Q = -6.0$ MeV) excited states of Ne^{20} respectively. Therefore the total reaction cross section is greater than at least 290 mb, which is about two times that for the first excited state. It is worthwhile to note that this total reaction cross section amounts to more than 60% of the nuclear geometrical cross section $\pi R^2 = 470$ mb with $R = 1.42 \times 10^{-13} \text{A}^{1/3} \text{ cm}$.

$\text{Mg}^{24}(p, p')\text{Mg}^{24*}$, $Q = -1.38$ MeV

This reaction has been studied already by many authors in the same energy region as that of the present work^{8), 11)}. Although the angular distribution shapes obtained by these authors change rather remarkably with proton energy, one can point out the typical distribution shapes which are most frequently found among them. This typical shape is of the type of the ones which are shown by Greenless and Souch at $E_p = 9.62$ MeV, by Fischer at 9.94 MeV, and by present authors at 13.9 MeV.

The magnitudes of the total cross sections of this reaction seem to be of the same order as those of the reaction to the first excited state of Ne^{20} .

As shown in Fig. 1(e), proton groups corresponding up to the eighth excited states of Mg^{24} reported in the literature¹⁹⁾ are observed well at $E_p = 14.1$ MeV. The total reaction cross section estimated from these yields is more than 42 mb/sterad. at $\theta_{\text{lab}} = 90^\circ$, about four times that for the first excited state reaction. Thus it is expected that the total reaction cross section would amount to an order of πR^2 , if the yield at $\theta_{\text{lab}} = 90^\circ$ roughly

† The results which were obtained in the present experiments for the angular distributions of the inelastically scattered protons exciting the higher states of Ne^{20} and other nuclei will be reported elsewhere.

represents the average differential cross section.

$\text{Si}^{28}(p, p')\text{Si}^{28*}, Q = -1.78 \text{ MeV}$

In the energy region of the present work, this reaction were studied by Greenlees et al.¹²⁾ at five values of energy from 7.97 to 9.45 MeV and also by Conzett at 12.0 MeV. The angular distributions obtained in the present work are different from each other and none of them has similarity with the results obtained by above authors. This fact shows that the angular distributions of the present reaction change remarkably with the energy. The excitation functions obtained at $\theta_{\text{lab}} = 45^\circ$ and 90° which are shown in Fig. 15(a) reveal this feature apparently. Here, it must be noted that the anomaly found at $E_p = 8.78 \text{ MeV}$ in Fig. 15(a) is also realized in the figure of the angular distribution reported by Greenless et al. as the variation of $\sigma(\theta_{\text{c.m.}} \simeq 45^\circ)$ with energy. Thus, as for the present reaction, in this energy region at least, the results obtained seem to support that the formation on the compound nucleus contributes effectively to the reaction.

During the course of writing the present paper, some of the present authors have studied the angular distributions at the anomaly point of 8.78 MeV and have obtained the distribution shape which is similar to that obtained by Greenless et al. at 8.96 MeV up to the backward scattering angle of 130° . The total cross section at this value of energy is 270 mb. These are included in Figs. 11 and 14.

The total cross section at 7.64 MeV is 316 mb and is larger than those at neighbouring energies which are about 230 mb at 7.97 MeV, and about 210 mb at 8.55 MeV estimated from the data by Greenless et al. Existence of an anomaly is expected near this value of energy, say, 7.64 MeV.

As is seen in Fig. 1(f), proton groups corresponding to the higher excited state of Si^{28} reported in the literature¹⁹⁾ are observed well at $E_p = 14.2 \text{ MeV}$. Among these groups, protons which arise from the reaction $\text{O}^{16}(p, p')\text{O}^{16*}(Q = -6.06, -6.14, -6.91 \text{ and } -7.12 \text{ MeV})$ are surely contained. Yet, the net yield for the total reactions by Si^{28} is several times that for the first excited state of Si^{28} . The total reaction cross section would therefore amount to the order of πR^2 .

$\text{S}^{32}(p, p')\text{S}^{32*}, Q = -2.14 \text{ MeV}$.

As has been described in § 4, the results obtained for this reaction in the present work reveal that the scattering features change itself gradually from this target nucleus to the heavier nuclei A^{40} and Ti . Namely the distribution shape in the lower energy region is rather flat and is almost symmetric about $\theta_{\text{c.m.}} = 90^\circ$. The shape seems also to change remarkably with energy up to 11 MeV, say. Above this energy, the change of the shape with energy would become smooth. Then at 14 MeV, the distribution shapes take the typical form which is seen in Figs. 12 and 13. The magnitudes of the total cross sections of this reaction shown in Fig. 15 seem generally to be smaller than those of the lighter nuclei (Ne^{20} , Mg^{24} and Si^{28}) and to be nearly equal to those of medium weight nuclei. As is shown in Fig. 1(g), proton groups corresponding to the higher excited states of S^{32} reported in the literature²¹⁾ are also observed at $E_p = 14 \text{ MeV}$. The total reaction cross section would therefore amount to several times that for the first state reaction; 57 mb.

$\text{A}^{40}(p, p')\text{A}^{40*}, Q = -1.46 \text{ MeV}$.

The results for this reaction obtained in the present work and the previously published works^{9), 14)} seem to reveal the following features. First, the angular distribution shapes do not change their principal patterns remarkably with proton energy. Secondly, the total cross sections of the reaction are extremely low compared with those obtained for the lighter even-even nuclei.

Both features which have been pointed out in the case of the target nucleus S^{32} are now recognized in the wide region of energy. Osaka group found, for example, at $E_p = 5.5 \text{ MeV}$ an angular distribution shape of this reaction similar to those at 7.77 and 9.31 MeV of the present work. The total cross section was 45 mb at 5.5 MeV.

As is seen in Fig. 1(h), proton groups corresponding to the higher excited state of A^{40} reported in the literature are observed at $E_p = 14.1 \text{ MeV}$. The total cross section to the first excited state is 32.5 mb. This value is, however, evidently smaller than those for the lighter nuclei; Ne^{20} , Mg^{24} , Si^{28} .

The features revealed above for A^{40} seem to be inherited by the succeeding even-even nuclei of medium weight such as titanium,

chromium, etc.

Thus it seems that A^{40} behaves, in the scattering of protons of medium energy, as the border-line nucleus between the light and the medium weight nuclei.

The even-even nuclei lighter than S^{32} which have been studied in the present work are all of $n\alpha$ -type ($Z=N=A/2=\text{even}$), but A^{40} has four excess neutrons. Moreover the separation energies of a proton in the compound nuclei composed of the former nuclei and a proton are small, being 2.29 MeV (Al^{25}) to 2.72 MeV (P^{29}), but the separation energy of a proton from K^{41} is 7.8 MeV. Owing to the same reason, the Q values of the (p, n) reactions are markedly different between both groups of nuclei. These differences in the natures of the target nuclei and in the conditions of the compound nuclei might be the reason for the marked differences in the scattering features of the light even-even nuclei and of A^{40} .

C. Summary

We summarize the results of the present experiment as follows.

i) The elastic scattering of protons by light nuclei shows generally the diffraction patterns in the region $E_p > 10$ MeV, but it changes with energy and with atomic number. The inelastic scattering of protons by light nuclei shows, on the other hand, angular distributions of variant features.

ii) The intensity of inelastic scattering from N^{14} ($Q = -2.31$ MeV and -3.95 MeV) is weak compared with those from other light even-even nuclei. This fact, especially in the case of $Q = -2.3$ MeV, seems to be a matter of significance.

iii) $E_p < 10$ MeV say, we find remarkable variations of the angular distribution shapes with energy for Ne^{20} , Mg^{24} , Si^{28} , and for S^{32} to some extent. Anomalies of resonance nature are expected at some values of energy for these nuclei. The existence of an anomaly with energy width of about 100 keV has been confirmed for $Si^{28}(p, p')Si^{28}$, $Q = -1.78$ MeV, at 8.78 MeV. The total cross sections of the reaction to the first excited states are large for these nuclei and for this energy region.

iv) In the higher energy region, $E_p > 12$ MeV, the total cross sections to the first excited states for even-even nuclei mentioned above decrease gradually with increasing

energy. The angular distribution shapes also seem to tend to some typical pattern characteristic to the nuclei. The typical shapes for Ne^{20} and Mg^{24} resemble each other. This is, however, not of the shape which is expected from the simple direct process theory using the Born approximation. The shapes for Si^{28} and S^{32} resemble each other and do not differ greatly from that of A^{40} . Finally the shape for A^{40} is similar to those for titanium and other medium weight nuclei, being the shape expected from the direct process theory with the Born approximation.

v) The inelastic scattering of protons from A^{40} , $Q = -1.46$ MeV, differs much from those for the lighter even-even nuclei over all the range of energy studied. This target nucleus seems to play a role of the border-line nucleus between the light and the medium weight nuclei in the scattering of protons. This features might have been caused by the differences of the structures of target nuclei with respect to the excess neutrons.

vi) The decreases mentioned in iv) of the total cross sections of the reactions leaving the nuclei in their first excited states are compensated with the gradual increases of the reaction cross sections corresponding to the higher excited states. The total reaction cross sections at $E_p = 14$ MeV amount to nearly the values of πR^2 , geometrical cross section of the nucleus, in the case of Ne^{20} , Mg^{24} and Si^{28} . These target nuclei are, therefore, nearly black for the impinging protons at this value of energy.

Acknowledgements

The authors are grateful to Professors I. Nonaka and S. Kikuchi for their encouragements throughout this work. They owe to Professor K. Saito for the preparation of gas targets. They say thanks to the INS cyclotron crew for their excellent operation.

References

- 1) M. Kondo and T. Yamazaki: J. Phys. Soc. Japan **13** (1958) 771.
- 2) Y. Oda, M. Takeda, C. Hu and S. Kato: J. Phys. Soc. Japan **14** (1959) 396.
- 3) S. Yamabe, M. Kondo, T. Yamazaki and A. Toi: J. Phys. Soc. Japan **13** (1958) 777.
- 4) Y. Oda, M. Takeda, C. Hu and S. Kato: J. Phys. Soc. Japan **14** (1959) 1255.
- 5) K. Kikuchi, S. Kobayashi and K. Matsuda:

- J. Phys. Soc. Japan **14** (1959) 121.
- 6) C. Hu, K. Kikuchi, S. Kobayashi, K. Matsuda, Y. Nagahara, Y. Oda, N. Takano, M. Takeka and T. Yamazaki: J. Phys. Soc. Japan **14** (1959) 861.
 - 7) R. G. Freemantle, D. J. Prowse, A. Hosain and J. Rotblat: Phys. Rev. **96** (1954) 1270.
 - 8) G. W. Greenless, B. C. Haywood, L. G. Kuo and M. Petravic: Proc. Phys. Soc. London **A, 70** (1957) 331.
 - 9) G. W. Greenless and A. E. Souch: Proc. Phys. Soc. London **A, 70** (1956) 331.
 - 10) G. E. Fischer: Phys. Rev. **96** (1954) 704.
 - 11) H. E. Conzett: Phys. Rev. **105** (1957) 1324.
 - 12) G. W. Greenless, L. G. Kuo, L. Lowe and M. Petrucci: Proc. Phys. Soc. London **71** (1958) 347.
 - 13) R. M. Fisberg and N. M. Hintz: Phys. Rev. **103** (1956) 645.
 - 14) Y. Oda, M. Takeda, C. Hu and S. Kato: unpublished.
 - 15) J. K. Bair, H. C. Cohn, J. D. Kington and H. B. Willard: Phys. Rev. **104** (1956) 1595.
 - 16) Y. Oda, M. Takeda, C. Hu and S. Kato: unpublished.
 - 17) C. K. Bockelman, C. P. Browne, W. W. Buchner and A. Sperduto: Phys. Rev. **92** (1953) 665.
 - 18) Banerjee, Levinson, Albright and Tobocmdu: Bull. Am. Phys. Soc. Ser. II, 1, see also. W.M. Visscher and R.A. Ferrell: Phys. Rev. **107** (1957) 781.
 - 19) P. M. Endt and J. C. Kluyver: Rev. Mod. Phys. **26** (1954) 95. For Ne²⁰, see Ref. 16).
 - 20) S. T. Butler: Phys. Rev. **106** (1957) 272.
 - 21) R. W. Peelle: Phys. Rev. **105** (1957) 1311.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

Radial Distribution Function of Fluids, III

By Kazuo HIROIKE

*Department of Physics, Tokyo Institute of Technology,
Oh-Okayama, Meguro, Tokyo*

(Received December 22, 1959)

A formula for the Helmholtz free energy of a one-component fluid, classical or quantum, is obtained in terms of the radial distribution function, by attaching a coupling constant to the pair interaction potential. Compatibility of the formula is discussed in connection with the formula derived in paper II, leading to the condition to be satisfied by the radial distribution function. It is shown that the condition for compatibility is equivalent in a classical fluid to the one discussed in paper I. The present formula is applied to deal with the hyper-netted chain approximation and the condition for compatibility is shown to be satisfied in this case. The formula is generalized to a multicomponent fluid and also to the case of a grand canonical ensemble.

§ 1. Introduction

In a classical fluid its pressure p and internal energy E can be calculated if the radial distribution function is known. (The radial distribution function will be hereafter abbreviated as the r.d.f.) Then the Helmholtz free energy A of the fluid is to be obtained in principle by integrating the equation

$$d\left(\frac{A}{T}\right) = -\frac{p}{T}dV - \frac{E}{T^2}dT,$$

where T and V denote the absolute temperature and the volume respectively.

In order that the right-hand side of the above equation is integrable, the pressure and internal energy must satisfy the relation

$$\frac{\partial}{\partial T}\left(\frac{p}{T}\right) = \frac{\partial}{\partial V}\left(\frac{E}{T^2}\right). \quad (1)$$

It is needless to say that the relation (1) is satisfied by the values of p and E which are calculated by the use of the exact r.d.f. It is, however, not always the case for some approximate r.d.f.'s. Even if the relation (1)

is not satisfied, we can calculate the free energy by integrating either p/T with respect to V or E/T^2 with respect to T . In such a case we obtain two different forms of the free energy. Therefore it can be said that the relation (1) is the condition to derive the free energy in a consistent way.

In paper I¹⁾ we examined such consistency of several approximate r.d.f.'s which were known up to that time. It was found that the original form of Green's linear theory is the only one which satisfies the relation (1). In paper II²⁾, changing a standpoint, we showed that the r.d.f. can be derived from the expression for the free energy if the latter is known as a functional of the pair interaction potential. We proved also that the relation (1) is satisfied by p and E which are based upon thus derived r.d.f.

Recently remarkable progress has been made in the theory of classical fluids by collecting particular terms from the virial expansion of the free energy or the r.d.f.³⁾⁻⁵⁾ Collecting particular terms is usually done more easily in the virial expansion of the r.d.f. than in that of the free energy. Such examples will be found in references 4) and 5). Therefore the method is desirable, by which the free energy can be calculated from the expression of the r.d.f.

To integrate p/T or E/T^2 is an example of such a method. However, that cannot be used in a quantum fluid, since the pressure and internal energy are not expressed in terms of the r.d.f. alone in the quantum fluid. The purpose of the present paper is to derive a formula by which the free energy is calculated from the known form of the r.d.f. in both the classical and quantum fluids and to

investigate the condition of consistency corresponding to the relation (1).

§ 2. Derivation of the Formula

Let us consider a classical fluid which is composed of N identical particles interacting with interaction potential U . The Helmholtz free energy is of the form:

$$\left. \begin{aligned} A &= -kT \log Q \\ Q &= \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z \\ Z &= \int \cdots \int_V dr_1 dr_2 \cdots dr_N e^{-U/kT}, \end{aligned} \right\} \quad (2)$$

where k , h and m have usual meanings. Now we consider a fictitious fluid in which the interaction potential is given by ξU . The free energy, configurational partition function and so on in such a fluid will be denoted by $A(\xi)$, $Z(\xi)$ and so on respectively. The quantities in the fluid with $\xi=0$ or in the fluid of free particles will be denoted by subscript letter 0. The parts of the quantities which are increased by the presence of the interaction will be denoted by subscript letter 1. (Such parts will be hereafter called the interaction parts.) For example $A(\xi)$ is written in the form

$$A(\xi) = A_0 + A_1(\xi). \quad (3)$$

From the definition the interaction part of the free energy can be written as

$$A_1(\xi) = \int_0^\xi d\xi \frac{dA(\xi)}{d\xi}.$$

Using expression (2) in which U is replaced by ξU , we obtain readily

$$A_1(\xi) = \int_0^\xi d\xi \langle U \rangle_\xi, \quad (4)$$

where

$$\langle U \rangle_\xi = \frac{1}{Z(\xi)} \int \cdots \int_V dr_1 dr_2 \cdots dr_N U e^{-\xi U/kT}. \quad (5)$$

We assume that U is the sum of the pair interaction potentials, that is,

$$U = \sum_{i>j}^N \sum_{j=1}^N \phi(r_{ij}). \quad (6)$$

Then Eq. (4) is reduced to

$$A_1(\xi) = N \frac{\rho}{2} \int_0^\xi d\xi \int dr \phi(r) g(r; \xi), \quad (7)$$

where ρ is the number density N/V . $g(r; \xi)$ is the r.d.f. of the fluid in which the pair interaction potential is given by $\xi\phi$, namely

$$g(|\mathbf{r}_1 - \mathbf{r}_2|; \xi) = \frac{1}{\rho^2} N(N-1) \frac{1}{Z(\xi)} \int \cdots \int_V d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\xi U/kT}. \quad (8)$$

Formula (7) is the one which we are looking for. Although the above derivation has been made in the classical fluid, formula (7) holds also in a quantum fluid. That can be readily verified by the use of the fact that Eq. (4) remains valid in the quantum fluid if $\langle U \rangle_\xi$ is defined by means of the density matrix in place of (5). Needless to say, the r.d.f. is defined in this case by

$$\left. \begin{aligned} g(|\mathbf{r} - \mathbf{r}'|; \xi) &= \frac{1}{\rho^2} \frac{1}{Q(\xi)} \text{Tr} \left[\sum_{i \neq j}^N \sum^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) e^{-(H_0 + \xi U)/kT} \right] \\ Q(\xi) &= \text{Tr} e^{-(H_0 + \xi U)/kT}, \end{aligned} \right\} \quad (8')$$

where H_0 is the Hamiltonian of free particles.

In the classical fluid the interaction part of the internal energy is

$$E_1(\xi) = \xi \langle U \rangle_\xi. \quad (9)$$

Therefore Eq. (4) is rewritten as

$$A_1(\xi) = \int_0^\xi \frac{d\xi}{\xi} E_1(\xi). \quad (10)$$

Since, as is seen from (5), $E_1(\xi)/kT$ depends on ξ and T only as $\xi U/kT$, Eq. (10) and hence Eq. (7) are equivalent to deriving the free energy by integrating the internal energy with respect to T . In the quantum fluid Eqs. (9) and (10) are not valid. There is nothing for it but to calculate $E_1(\xi)$ by the use of the thermodynamical relation

$$E_1(\xi) = -T^2 \frac{\partial}{\partial T} \left(\frac{A_1(\xi)}{T} \right). \quad (11)$$

It should be noted that $g(r; \xi)$ appearing in (7) is different from the r.d.f. appearing in Kirkwood's integral equation⁶⁾. The latter is the r.d.f. of the fluid in which the pair interaction potentials between a specified particle and the other particles are given by $\xi\phi$ and the other pair interaction potentials remain ϕ . On the contrary, all the pair interaction potentials are $\xi\phi$ in our case.

§ 3. Investigation of Compatibility

If we know the r.d.f., we can calculate the free energy by means of formula (7). On the other hand, as has been shown in paper II²⁾, the r.d.f. can be derived from the free energy. In order that formula (7) is used in a compatible way, we must obtain the r.d.f. identical to that used at first in the right-hand side of (7) if we derive the r.d.f. conversely from the free energy given by (7). The condition for that will be found in the present section. It will be also shown that if the condition is satisfied in a classical fluid, the values of p and E calculated by means of the r.d.f. satisfy relation (1).

As shown in paper II²⁾, we have the following relation between the r.d.f. and the free energy:

$$g(r) = \frac{1}{N} \frac{2}{\rho} \left(\frac{\partial A}{\partial \phi} \right)_r. \quad (12)$$

$(\partial/\partial\phi)_r$ -operation is a kind of functional derivative which is defined as follows. The pair interaction potential ϕ is varied by $\Delta\phi$ in a quantity $F[\phi(r')]$, being functional of ϕ . The corresponding first order variation, with respect to $\Delta\phi$, of F is denoted by $f[\Delta\phi(r')]$, which is a linear functional of $\Delta\phi$ by definition. Then $(\partial F/\partial\phi)_r$ is defined by

$$\left(\frac{\delta F}{\delta \phi}\right)_r = f[\delta(r-r')] .$$

When the pair interaction potential is $\xi\phi$, (12) is written as

$$g(r; \xi) = \frac{1}{N} \frac{2}{\rho} \frac{1}{\xi} \left(\frac{\delta A_1(\xi)}{\delta \phi} \right)_r , \quad (12')$$

where we have used $A_1(\xi)$ instead of $A(\xi)$, since A_0 is independent of the interaction.

Our purpose is to seek the condition for the compatibility of Eqs. (12') and (7). Substitution of (7) into the right-hand side of (12') leads to

$$\begin{aligned} g(r; \xi) &= \frac{1}{\xi} \int_0^\xi d\eta \int dr' \left[\left(\frac{\delta \phi(r')}{\delta \phi} \right)_r g(r'; \eta) + \phi(r') \left(\frac{\delta g(r'; \eta)}{\delta \phi} \right)_r \right] \\ &= \frac{1}{\xi} \int_0^\xi d\eta \int dr' \left[\delta(r-r') g(r'; \eta) + \phi(r') \left(\frac{\delta g(r'; \eta)}{\delta \phi} \right)_r \right] . \end{aligned}$$

This can be written as

$$\xi g(r; \xi) = \int_0^\xi d\eta g(r; \eta) + \int_0^\xi d\eta \int dr' \phi(r') \left(\frac{\delta g(r'; \eta)}{\delta \phi} \right)_r .$$

Differentiating this equation with respect to ξ , we obtain finally

$$\xi \frac{\partial g(r; \xi)}{\partial \xi} = \int dr' \phi(r') \left(\frac{\partial g(r'; \xi)}{\partial \phi} \right)_r . \quad (13)$$

That is the necessary condition of being compatible of (12') and (7). It is easy to prove that Eq. (13) is also the sufficient condition. Therefore we may say that Eq. (13) is the condition which we are seeking.

Though the condition (13) of compatibility can be applied to both classical and quantum fluids, we shall here consider classical fluids. When the r.d.f. satisfies (13), the values of p and E calculated by the use of this r.d.f. satisfy the relation (1). That will be proved in the following. The interaction parts of p and E are expressed respectively as⁷⁾

$$p_1(\xi) = -\frac{\rho^2}{6} \int dr \xi r \cdot \frac{\partial \phi(r)}{\partial r} g(r; \xi) \quad (14)$$

and

$$E_1(\xi) = N \frac{\rho}{2} \int dr \xi \phi(r) g(r; \xi) . \quad (15)$$

We are to prove that the relation

$$\frac{\partial}{\partial T} \left(\frac{p_1(\xi)}{T} \right) = \frac{\partial}{\partial V} \left(\frac{E_1(\xi)}{T^2} \right) \quad (16)$$

is satisfied by $p_1(\xi)$ and $E_1(\xi)$ which are given by (14) and (15) respectively.

Following the definition of $(\delta/\delta\phi)_r$ -operation, we write as

$$\left(\frac{\delta g(r'; \xi)}{\delta \phi} \right)_r \equiv G[r'; \delta(r-r')] . \quad (17)$$

By definition $G[r'; \delta(r-r')]$ is a linear functional of $\delta(r-r')$. We assume that the r.d.f. is dependent on T and V only as the form shown explicitly in the following:

$$g(r; \xi) = g \left[\frac{\xi \phi(Lx)}{kT}, \frac{\xi \phi(Lx')}{kT} \right] , \quad (18)$$

where $V \equiv L^3$, $r \equiv Lx$, $r' \equiv Lx'$ and $\xi \phi(Lx')/kT$ is written to show that g is a functional

of it. This assumption will not lose us the generality of our proof, since such a form of the r.d.f. is in general expected from a dimension consideration.

From (14) and (18) we obtain readily

$$\frac{\partial}{\partial T} \left(\frac{p_1(\xi)}{T} \right) = -\frac{p_1(\xi)}{T^2} + \frac{\rho^2}{6T^2} \int d\mathbf{r} \, \xi \, \mathbf{r} \cdot \frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \left\{ \xi \frac{\partial}{\partial \xi} g(\mathbf{r}; \xi) \right\}. \quad (19)$$

Remembering the way of defining the functional G (see below Eq. (12)), we obtain, with the aid of (15), (17) and (18),

$$\begin{aligned} \frac{\partial E_1(\xi)}{\partial V} &= \frac{L}{3V} \frac{\partial}{\partial L} E_1(\xi) \\ &= \frac{N^2}{6} \frac{L}{V} \int d\mathbf{x}' \, \xi \left\{ \mathbf{x}' \cdot \frac{\partial \phi(\mathbf{r}')}{\partial \mathbf{r}'} g(\mathbf{r}'; \xi) + \phi(\mathbf{r}') G \left[\mathbf{r}'; \mathbf{x}'' \cdot \frac{\partial \phi(\mathbf{r}'')}{\partial \mathbf{r}''} \right] \right\} \\ &= \frac{\rho^2}{6} \int d\mathbf{r}' \, \xi \left\{ \mathbf{r}' \cdot \frac{\partial \phi(\mathbf{r}')}{\partial \mathbf{r}'} g(\mathbf{r}'; \xi) + \phi(\mathbf{r}') G \left[\mathbf{r}'; \mathbf{r}'' \cdot \frac{\partial \phi(\mathbf{r}'')}{\partial \mathbf{r}''} \right] \right\} \\ &= -p_1(\xi) + \frac{\rho^2}{6} \int d\mathbf{r} \int d\mathbf{r}' \, \xi \phi(\mathbf{r}') \mathbf{r} \cdot \frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} G[\mathbf{r}'; \delta(\mathbf{r}-\mathbf{r}')] \\ &= -p_1(\xi) + \frac{\rho^2}{6} \int d\mathbf{r} \int d\mathbf{r}' \, \xi \phi(\mathbf{r}') \mathbf{r} \cdot \frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \left(\frac{\partial g(\mathbf{r}'; \xi)}{\partial \phi} \right)_r. \end{aligned}$$

After all we obtain

$$\frac{\partial}{\partial V} \left(\frac{E_1(\xi)}{T^2} \right) = -\frac{p_1(\xi)}{T^2} + \frac{\rho^2}{6T^2} \int d\mathbf{r} \, \xi \, \mathbf{r} \cdot \frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \int d\mathbf{r}' \, \phi(\mathbf{r}') \left(\frac{\partial g(\mathbf{r}'; \xi)}{\partial \phi} \right)_r. \quad (20)$$

Therefore if $g(\mathbf{r}; \xi)$ satisfies Eq. (13), the right-hand sides of (19) and (20) are equal to each other and hence relation (16) has been proved.

§ 4. Example

As an application of (7) we shall deal with the hyper-netted chain approximation proposed by Morita³⁾. It has been shown in reference 4) that the r.d.f. in this approximation can be found by means of comparatively simple consideration. When the r.d.f. is written in the form

$$g(\mathbf{r}) = \exp \left[-\frac{\phi(\mathbf{r})}{kT} + h(\mathbf{r}) \right], \quad (21)$$

the function $h(\mathbf{r})$ in the hyper-netted chain approximation is the solution of a set of two equations:

$$H(\mathbf{k}) = \frac{\rho F^2(\mathbf{k})}{1 - \rho F(\mathbf{k})} \quad (22)$$

and

$$f(\mathbf{r}) = [b(\mathbf{r}) + 1] e^{b(\mathbf{r})} - 1 - h(\mathbf{r}), \quad (23)$$

where

$$b(\mathbf{r}) = e^{-\phi(\mathbf{r})/kT} - 1. \quad (24)$$

In Eq. (22) $H(\mathbf{k})$ is the Fourier transform of $h(\mathbf{r})$, that is

$$\left. \begin{aligned} H(\mathbf{k}) &= \int d\mathbf{r} \, h(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} \\ h(\mathbf{r}) &= \frac{1}{V} \sum_{\mathbf{k}} H(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}}, \end{aligned} \right\} \quad (25)$$

and hence

and $F(k)$ is the Fourier transform of $f(r)$.

When the pair interaction potential is $\xi\phi$, the functions $g(r)$, $h(r)$, $F(k)$ and so on will be denoted by $g(r; \xi)$, $h(r; \xi)$, $F(r; \xi)$ and so on respectively, as before. Relations similar to (21)–(25) hold among these functions depending on ξ . By the use of the relations similar to (21) and (24), we obtain

$$\phi(r)g(r; \xi) = -kT \frac{\partial h(r; \xi)}{\partial \xi} e^{h(r; \xi)}. \quad (26)$$

Differentiation of the equation similar to (23) with respect to ξ gives us the relation

$$\frac{\partial h(r; \xi)}{\partial \xi} e^{h(r; \xi)} = \frac{\partial}{\partial \xi} \left\{ f(r; \xi) - f(r; \xi) h(r; \xi) - \frac{1}{2} h^2(r; \xi) \right\} + h(r; \xi) \frac{\partial f(r; \xi)}{\partial \xi} \quad (27)$$

Furthermore we obtain, with the aid of the equation similar to (22),

$$H(k; \xi) \frac{\partial F(k; \xi)}{\partial \xi} = -\frac{1}{\rho^2} \frac{\partial}{\partial \xi} \left\{ \log(1 - \rho F(k; \xi)) + \rho F(k; \xi) + \frac{1}{2} \rho^2 F^2(k; \xi) \right\}. \quad (28)$$

Using (26), (27) and (28), we obtain, after a straightforward calculation,

$$\int dr \phi(r) g(r; \xi) = kT \frac{\partial}{\partial \xi} \left[-\int dr f(r; \xi) + \frac{1}{\rho^2} \frac{1}{V} \sum_k \left\{ \log(1 - \rho F(k; \xi)) + \rho F(k; \xi) + \frac{\rho^2}{2} (F(k; \xi) + H(k; \xi))^2 \right\} \right].$$

For convenience of the later calculation the first term on the right-hand side is rewritten by the use of the equations similar to (23) and (24). Then the above expression is written as

$$\begin{aligned} \int dr \phi(r) g(r; \xi) = kT \frac{\partial}{\partial \xi} \left[-\int dr \left\{ \exp \left[-\frac{\xi \phi(r)}{kT} + h(r; \xi) \right] - 1 - h(r; \xi) \right\} \right. \\ \left. + \frac{1}{\rho^2} \frac{1}{V} \sum_k \left\{ \log(1 - \rho F(k; \xi)) + \rho F(k; \xi) + \frac{\rho^2}{2} (F(k; \xi) + H(k; \xi))^2 \right\} \right]. \end{aligned} \quad (29)$$

When Eq. (29) is substituted into formula (7), the interaction part of the free energy in the hyper-netted chain approximation is obtained as follows:

$$\begin{aligned} \frac{A_1}{NkT} = -\frac{\rho}{2} \int dr \left[\exp \left(-\frac{\phi(r)}{kT} + h(r) \right) - 1 - h(r) \right] \\ + \frac{1}{2\rho} \frac{1}{V} \sum_k \left[\log \{1 - \rho F(k)\} + \rho F(k) + \frac{\rho^2}{2} \{F(k) + H(k)\}^2 \right], \end{aligned} \quad (30)$$

where we have used the fact that $h=H=f=F=0$ at $\xi=0$. This expression is just the one which has been used by Morita⁴⁾ to demonstrate the variational principle of the free energy in the hyper-netted chain approximation.

The r.d.f. in the hyper-netted chain approximation satisfies relation (13). That is directly verified as follows. From the definition of $(\delta/\delta\phi)_r$ -operation we have the relation

$$\left(\frac{\delta}{\delta\phi} \int dr' \phi(r') g(r'; \xi) \right)_r = g(r; \xi) + \int dr' \phi(r') \left(\frac{\delta g(r'; \xi)}{\delta\phi} \right)_r. \quad (31)$$

On the other hand, if use is made of Eq. (29), we obtain

$$\begin{aligned} \left(\frac{\partial}{\partial \phi} \int dr' \phi(r') g(r'; \xi) \right)_r = kT \frac{\partial}{\partial \xi} \left[-\frac{\xi}{kT} \exp \left(-\frac{\xi \phi(r)}{kT} + h(r; \xi) \right) \right. \\ \left. - \int dr' \left\{ \exp \left(-\frac{\xi \phi(r')}{kT} + h(r'; \xi) \right) - 1 - h(r'; \xi) - f(r'; \xi) \right\} \left(\frac{\partial h(r'; \xi)}{\partial \phi} \right)_r \right. \\ \left. + \frac{1}{\rho} \frac{1}{V} \sum_k \left\{ -\frac{1}{1 - \rho F(k; \xi)} + 1 + \rho F(k; \xi) + \rho H(k; \xi) \left(\frac{\partial F(k; \xi)}{\partial \phi} \right)_r \right\} \right]. \end{aligned}$$

Both the coefficients of $(\partial h(r'; \xi)/\partial \phi)_r$ and $(\partial F(k; \xi)/\partial \phi)_r$ in the above expression are identically zero by the use of (23) and (22). Therefore the right-hand side of the above expression is written as

$$\begin{aligned} \frac{\partial}{\partial \xi} \left[\xi \exp \left(-\frac{\xi \phi(r)}{kT} + h(r; \xi) \right) \right] = \frac{\partial}{\partial \xi} [\xi g(r; \xi)] \\ = g(r; \xi) + \xi \frac{\partial g(r; \xi)}{\partial \xi}. \end{aligned}$$

Equating this expression to the right-hand side of (31), we obtain the relation (13), that is to say, the relation (13) has been proved in the hyper-netted chain approximation. The following fact also shows that the relation (13) holds in this approximation. By the use of relation (12) we can derive the r.d.f. from (30). The result is

$$\frac{1}{N} \frac{2}{\rho} \left(\frac{\partial A_1}{\partial \phi} \right)_r = \exp \left[-\frac{\phi(r)}{kT} + h(r) \right].$$

The right-hand side is just the r.d.f. in the hyper-netted chain approximation. This fact has been pointed out by Morita⁴⁾.

§ 5. Generalization of the Formula

We have so far considered the one-component fluid alone. Formula (7) can be generalized in quite a straightforward way to a multicomponent fluid. In the σ -component fluid there exists the formula

$$A_1(\xi) = \frac{V}{2} \int_0^\xi d\xi \int dr \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_{\alpha} \rho_{\beta} \phi_{\alpha\beta}(r) g_{\alpha\beta}(r; \xi), \quad (32)$$

where ρ_{α} (ρ_{β}) denotes the number density of α (β)-species, and $\phi_{\alpha\beta}(r)$ and $g_{\alpha\beta}(r; \xi)$ denote the pair interaction potential and the r.d.f. between α -species and β -species, respectively.

Finally we shall derive the formula in a grand canonical ensemble. For brevity we shall again consider the one-component fluid. If use is made of the formalism of the second quantization, the pressure, being supposed to be a function of T , V and λ , is given by

$$\left. \begin{aligned} p &= \frac{kT}{V} \log \Xi \\ \Xi &= \text{Tr } \lambda^N e^{-(H_0 + U)/kT} \end{aligned} \right\} \quad (33)$$

H_0 is the Hamiltonian of free particles. The interaction potential U is written in terms of the quantized wave functions as

$$U = \frac{1}{2} \iint dx dx' \Psi^+(x) \Psi^+(x') \phi(|\mathbf{r} - \mathbf{r}'|) \Psi(x') \Psi(x), \quad (34)$$

where we have denoted the spatial and spin coordinates together by x or x' .

In a similar way as in § 2 we obtain

$$\frac{dp(\xi)}{d\xi} = -\frac{1}{V} \frac{1}{\Xi(\xi)} \text{Tr } U \lambda^N e^{-(H_0 + \xi U)/kT},$$

If we define the pair distribution function $\rho^{(2)}(r; \xi)$ by

$$\rho^{(2)}(r; \xi) = \frac{1}{V} \frac{1}{\Xi(\xi)} \text{Tr} \left\{ \iint dx_1 dx_2 \Psi^+(x_1) \Psi^+(x_2) \delta(r - r_1 + r_2) \Psi(x_2) \Psi(x_1) \lambda^N e^{-(H_0 + \xi U)/kT} \right\}, \quad (35)$$

the formula corresponding to (7) in the grand canonical ensemble is written in the form*:

$$\begin{aligned} p_1(\xi) &= \int_0^\xi d\xi \frac{dp(\xi)}{d\xi} \\ &= -\frac{1}{2} \int_0^\xi d\xi \int dr \phi(r) \rho^{(2)}(r; \xi). \end{aligned} \quad (36)$$

Needless to say, the pair distribution function is related with the r.d.f. by

$$\rho^{(2)}(r) = \rho^2 g(r), \quad (37)$$

where ρ is to be supposed as the average number density over the grand canonical ensemble. It should be noted that ρ is a function of ξ if the pair interaction potential is given by $\xi\phi$, namely

$$\rho^{(2)}(r; \xi) = \rho^2(\xi) g(r; \xi). \quad (37')$$

A part of this work was supported by the Scientific Research Expenditure of the Ministry of Education.

References

- 1) K. Hiroike: J. Phys. Soc. Japan **12** (1957) 326.
- 2) K. Hiroike: J. Phys. Soc. Japan **12** (1957) 864.
- 3) K. Hiroike: J. Phys. Soc. Japan **13** (1958) 1497.
R. Abe: J. Phys. Soc. Japan **14** (1959) 10;
Progr. Theor. Phys. **22** (1959) 213. T. Morita:
Progr. Theor. Phys. **20** (1958) 920; **21** (1959)
361. E. Meeron: J. Chem. Phys. **28** (1958)
630; Phys. Fluids **1** (1958) 139. E. Meeron and
E. R. Rodemich: Phys. Fluids (1958) 246.
H. L. Friedman: Molecular Phys. **2** (1959) 23.
- 4) T. Morita: Progr. Theor. Phys. **23** (1960) 175
and No. 5.
- 5) T. Morita and K. Hiroike: Progr. Theor. Phys.
23 (1960) 385 and No. 6.
- 6) J. G. Kirkwood: J. Chem. Phys. **3** (1935) 300.
J. G. Kirkwood and E. M. Boggs: J. Chem.
Phys. **10** (1942) 394.
- 7) T. L. Hill: *Statistical Mechanics* (McGraw-
Hill, New York, 1956) pp. 189 and 190.

* After the manuscript had been written, the author noticed of the fact that Kanazawa and Watabe have derived the formula equivalent to (36). (H. Kanazawa and M. Watabe: Progr. Theor. Phys. **22** (1959) 466.)

Expansion Theorem of Density Matrix, Virial Expansion and New Formula of Multiple Scattering

By Toshio YOKOTA

The Institute of Statistical Mathematics, Tokyo

(Received December 23, 1959)

Expansion formulas for density matrices are derived with the use of the calculus of ordered exponentials. Using the formulas the expressions for virial coefficients are explicitly obtained. The expression of the third virial coefficient is calculated to obtain its expansion formula in terms of $\hbar^2\beta/M$. The expansion formulas for density matrices can be used to derive a new formula of multiple scattering, which involves Luttinger and Kohn's formula as a special case. The expansion formula for the normalized density matrix is also given. Expansion formulas which are to be applied to irreversible processes and relaxation phenomena are also given.

§ 1. Introduction

In classical statistical mechanics, as is well known, the virial expansion theory is completely formulated by Mayer¹⁾ and others, and the 2nd, 3rd and 4th virial coefficients have been calculated by many authors for some types of potential, e.g., Lennard-Jone's type, well type, and some core models. Their numerical values and comparison with experimental data are seen in the textbook by Hirshfelder, Curtiss and Bird²⁾ and in Kihara's papers³⁾. In quantum statistical mechanics, the 2nd virial coefficient has been calculated but the 3rd virial coefficient is known only at high temperature. These numerical results are also found in the aforementioned literatures.

In quantum statistical mechanics, the virial expansion theory has been introduced first by Kahn and Uhlenbeck. In Section 2 the expansion theorem of the density matrix is derived as an extension of Mayer's theory to quantum statistical mechanics. In Section 3 the formula of the 3rd as well as the 2nd virial coefficient is given. It is further shown that the expansion formula in power series of $\hbar^2\beta/M$ is found by the modified method of Goldberger and Adams⁴⁾, and the 2nd term of this series agrees with the result of Kihara, Mizuno and Shizume. In Appendix B higher virial coefficients are also derived.

When a perturbing potential consists of two body forces, Watson attempted to calculate the virial coefficients by use of the multi-

ple scattering formula⁵⁾, but he succeeded in finding only the 2nd virial coefficient. This indicates that the usual formula for multiple scattering is useful only to treat double collisions. In Section 4 we shall give a new formula for multiple scattering which is classified by multiple collisions, i.e., double collisions, triple collisions,...etc., when the interaction potential consists of many body forces. In the particular case when the potential consists of one body forces, our formula agrees with Luttinger and Kohn's.⁶⁾ In Section 5, by use of this formula, the expansion formula of normalized density matrix is given, and it is shown that the normalization factor should be chosen carefully. In Section 6 we shall show the formulas which are applied to irreversible processes and relaxation phenomena.

§ 2. Expansion Theorem for Density Matrix

In the usual perturbation scheme in quantum mechanics the motion of a perturbed system whose Hamiltonian V with respect to an unperturbed system with Hamiltonian H_0 is expressed by the interaction representation, i.e.,

$$V(s) = \exp(sH_0)V\exp(-sH_0). \quad (2.1)$$

Therefore the correct expansion formula of the density matrix is obtained by expanding the interaction representation $V(s)$ in the same way as in classical statistical mechanics. The following expansion theorem for density matrix satisfies this requirement.

Theorem If the expansion formula for the operator $\exp(-\beta V)$ is represented by a series

of exponential operators, the expansion of $\exp(-\beta(H_0 + V))$ is obtained by adding H_0 into every exponential and replacing 1 by $\exp(-\beta H_0)$ in the expansion formula of $\exp(-\beta V)$.

For an example of this theorem, we shall derive the following usual formula as an extension of Mayer's expansion formula in classical statistical mechanics.

Formula If V is divided arbitrarily into some parts, i.e., $V = \sum_{\alpha} V_{\alpha}$, then

$$\begin{aligned} \exp(-\beta(H_0 + V)) &= \exp(-\beta H_0) + \sum_{\alpha} \{ \exp(-\beta(H_0 + V_{\alpha})) - \exp(-\beta H_0) \} \\ &\quad + \sum_{\alpha < \beta} \{ \exp(-\beta(H_0 + V_{\alpha} + V_{\beta})) - \exp(-\beta(H_0 + V_{\alpha})) \\ &\quad - \exp(-\beta(H_0 + V_{\beta})) + \exp(-\beta H_0) \} + \cdots \end{aligned} \quad (2.2)$$

This is easily seen by use of the formula

$$\exp(-\beta(H_0 + V)) = \exp(-\beta H_0) \exp_+ \left(- \int_0^{\beta} ds V(s) \right), \quad (2.3)$$

where $V(s)$ is the interaction representation of the potential V and is defined by Eq. (2.1). If we introduce the symbol $(\)_+$ which denotes chronological ordering, the ordered exponential becomes

$$\exp_+ \left(- \int_0^{\beta} ds V(s) \right) = \left(\exp \left(- \sum_{\alpha} \int_0^{\beta} ds V_{\alpha}(s) \right) \right)_+, \quad (2.4)$$

and the operator in the parenthesis $(\)_+$ may be treated like c -number;

$$\left(\exp \left(- \sum_{\alpha} \int_0^{\beta} ds V_{\alpha}(s) \right) \right)_+ = \left(\prod_{\alpha} (1 + f_{\alpha}) \right)_+, \quad (2.5)$$

where

$$f_{\alpha} = \exp \left(- \int_0^{\beta} ds V_{\alpha}(s) \right) - 1.$$

The above equation can be expanded in the same manner as that Mayer used in classical statistical mechanics:

$$\begin{aligned} \exp_+ \left(- \int_0^{\beta} ds V(s) \right) &= (1 + \sum_{\alpha} f_{\alpha} + \sum_{\alpha < \beta} f_{\alpha} f_{\beta} + \sum_{\alpha < \beta < \gamma} f_{\alpha} f_{\beta} f_{\gamma} + \cdots)_+ \\ &= 1 + \sum_{\alpha} (f_{\alpha})_+ + \sum_{\alpha < \beta} (f_{\alpha} f_{\beta})_+ + \sum_{\alpha < \beta < \gamma} (f_{\alpha} f_{\beta} f_{\gamma})_+ + \cdots \end{aligned} \quad (2.6)$$

This is the expansion of $V(s)$ and satisfies the above mentioned requirement. If we put Eq. (2.6) into Eq. (2.3) using Eqs. (2.5) and (2.4) and return the ordered exponential to usual exponential, then we get the following terms from the series in Eq. (2.6).

The 1st term:

$$\exp(-\beta H_0) 1 = \exp(-\beta H_0).$$

The 2nd term:

$$\begin{aligned} \exp(-\beta H_0) \sum_{\alpha} (f_{\alpha})_+ &= \sum_{\alpha} \exp(-\beta H_0) \left(\exp_+ \left(- \int_0^{\beta} ds V(s) \right) - 1 \right) \\ &= \sum_{\alpha} \{ \exp(-\beta(H_0 + V_{\alpha})) - \exp(-\beta H_0) \}. \end{aligned}$$

The 3rd term:

$$\begin{aligned} \exp(-\beta H_0) \sum_{\alpha < \beta} (f_{\alpha} f_{\beta})_+ &= \sum_{\alpha < \beta} \exp(-\beta H_0) \left(\exp_+ \left(- \int_0^{\beta} ds (V_{\alpha}(s) + V_{\beta}(s)) \right) \right. \\ &\quad \left. - \exp_+ \left(- \int_0^{\beta} ds V_{\alpha}(s) \right) - \exp_+ \left(- \int_0^{\beta} ds V_{\beta}(s) \right) + 1 \right) \end{aligned}$$

$$= \sum_{\alpha < \beta} \{ \exp(-\beta(H_0 + V_\alpha + V_\beta)) - \exp(-\beta(H_0 + V_\alpha)) - \exp(-\beta(H_0 + V_\beta)) + \exp(-\beta H_0) \} . \quad (2.7)$$

etc.

Each of the terms in the above equation is appearing in the right side of Eq. (2.2).

From this example it is easily seen that the above theorem holds.

§ 3. Virial Expansion

We shall now consider the virial expansion for an imperfect gas consisting of N identical molecules which have kinetic energy $H_0 = \sum_{i=1}^N K_i = \sum_i (\hbar^2/2M) \nabla_i \cdot \nabla_i$ and which interact mutually with the following interaction potential V ,

$$V = \sum_{i < j} V_{ij}^{(2)} + \sum_{i < j < k} V_{ijk}^{(3)} + \dots , \quad (3.1)$$

where $V_{ij}^{(2)}$ is the two body force between the i -th and the j -th molecules, $V_{ijk}^{(3)}$ is the three body force between the i -th, the j -th and the k -th molecules, ...etc. If we put Eq. (3.1) into Eq. (2.2) and rearrange it in such a way that the 1st term contains no interacting parts, the 2nd two-particle interactions, and so on. The series is thus arranged by the number of two particle interactions, and by the number of three particle interactions and mixed order of the two and three particle interaction, and so on. We obtain

$$\begin{aligned} & \exp(-\beta(H_0 + V)) \\ &= \prod_{h=1}^N A^{(1)}(h) + \sum_{i < j} A^{(2)}(ij) \prod_{h \neq i, j} A^{(1)}(h) + \sum_{(i < j) \neq (k < l)} A^{(2)}(ij) A^{(2)}(kl) \prod_{h \neq i, j, k, l} A^{(1)}(h) + \dots \\ &+ \sum_{i < j < k} A^{(3)}(ijk) \prod_{h \neq i, j, k} A^{(1)}(h) + \dots \\ &+ \dots , \end{aligned} \quad (3.2)$$

where

$$\begin{aligned} A^{(1)}(h) &= \exp(-\beta K_h) = \rho^{(1)}(h) , \\ A^{(2)}(ij) &= \rho^{(2)}(ij) - \rho^{(1)}(i) \rho^{(1)}(j) , \\ A^{(3)}(ijk) &= \rho^{(3)}(ijk) - \rho^{(1)}(i) \rho^{(2)}(jk) - \rho^{(1)}(j) \rho^{(2)}(ik) - \rho^{(1)}(k) \rho^{(2)}(ij) + 2\rho^{(1)}(i) \rho^{(1)}(j) \rho^{(1)}(k) , \text{ etc.} \\ \rho^{(2)}(ij) &= \exp(-\beta(K_i + K_j + V_{ij}^{(2)})) , \\ \rho^{(3)}(ijk) &= \exp(-\beta(K_i + K_j + K_k + V_{ijk}^{(3)} + V_{ij}^{(2)} + V_{jk}^{(2)} + V_{ki}^{(2)})) , \text{ etc.} \end{aligned} \quad (3.2')$$

$A^{(2)}(ij)$ denotes the double collision between the i -th and the j -th molecules, and $A^{(3)}(ijk)$ denotes the triple collision between the i -th, the j -th and the k -th molecules, and so on. Another proof of the above theorem is easily seen by use of the theorem in the previous section.

As is well known, the free energy F is given by the relation

$$\exp(-\beta F) = \text{Tr} \{ \exp(-\beta(H_0 + V)) \delta_{qu}^{(N)} \} / N! , \quad (3.3)$$

where $\delta_{qu}^{(N)}$ denotes the permanent or determinant of N δ -functions according to Einstein-Bose or Fermi-Dirac statistics, i.e.,

$$\delta_{qu}^{(N)} = \begin{vmatrix} \delta(\mathbf{x}_1 - \mathbf{x}_1') & \dots & \delta(\mathbf{x}_1 - \mathbf{x}_{N'}) \\ \vdots & & \vdots \\ \delta(\mathbf{x}_N - \mathbf{x}_{N'}) & \dots & \delta(\mathbf{x}_N - \mathbf{x}_{N'}) \end{vmatrix}_{\pm} , \quad (3.4)$$

and Tr is such a symbol that after operating $\exp(-\beta(H_0 + V))$ on the function $\delta_{qu}^{(N)}$, the parameters $\mathbf{x}_1', \dots, \mathbf{x}_{N'}$ are identified with the variables $\mathbf{x}_1, \dots, \mathbf{x}_N$, respectively, and the multi-

ple integration with respect to $\mathbf{x}_1, \dots, \mathbf{x}_N$ is performed. Hereafter the symbol Tr is used in this way and the double signature is such that the upper signature is the case of Einstein-Bose statistics and the lower signature is the case of Fermi-Dirac statistics.

The function $\delta_{qu}^{(N)}$ is expanded in the same manner as the expansion of Eq. (3.2), i.e.,

$$\begin{aligned} \delta_{qu}^{(N)} = & \prod_{h=1}^N \delta^{(1)}(h) \pm \sum_{i < j} \delta^{(2)}(ij) \prod_{h \neq i, j} \delta^{(1)}(h) + \sum_{(i < j) \neq (k < l)} \delta^{(2)}(ij) \delta^{(2)}(kl) \prod_{h \neq i, j, k, l} \delta^{(1)}(h) + \dots \\ & + \sum_{i < j < k} \delta^{(3)}(ijk) \sum_{h \neq i, j, k} \delta^{(1)}(h) + \dots \\ & + \dots, \end{aligned} \quad (3.5)$$

where

$$\begin{aligned} \delta^{(1)}(h) &= \delta(\mathbf{x}_h - \mathbf{x}_{h'}) \\ \delta^{(2)}(ij) &= \delta(\mathbf{x}_i - \mathbf{x}_{j'}) \delta(\mathbf{x}_j - \mathbf{x}_{i'}) \\ \delta^{(3)}(ijk) &= \delta(\mathbf{x}_i - \mathbf{x}_{j'}) \delta(\mathbf{x}_j - \mathbf{x}_{k'}) \delta(\mathbf{x}_k - \mathbf{x}_{i'}) + \delta(\mathbf{x}_i - \mathbf{x}_{k'}) \delta(\mathbf{x}_k - \mathbf{x}_{j'}) \delta(\mathbf{x}_j - \mathbf{x}_{i'}) \text{ etc.} \end{aligned} \quad (3.5')$$

The above relation is easily seen from the definition of $\delta_{qu}^{(N)}$ and its derivation is shown in Appendix A.

Now if we put Eqs. (3.2) and (3.5) into Eq. (3.3) and rearrange it in the same way as Eq. (3.2), we obtain

$$\begin{aligned} \exp(-\beta F) = & \frac{1}{N!} \frac{\Omega^N}{v_0^N} \left\{ 1 + \frac{N-1}{2} d \frac{v_0^2}{\Omega} (W^{(2)}(2; 1, 1) \pm W^{(2)}(2; 2) \pm W^{(2)}(1, 1; 2)) \right. \\ & + \frac{1}{2} \left(\left(\frac{N-1}{2} \right)^2 - \frac{(N-1)(N-3/2)}{N} \right) d^2 \frac{v_0^4}{\Omega^2} (W^{(2)}(2; 1, 1) \\ & \quad \pm W^{(2)}(2; 2) \pm W^{(2)}(1, 1; 2))^2 + \dots \\ & + \frac{(N-1)(N-2)}{6N} d^2 \frac{v_0^3}{\Omega} (W^{(3)}(3; 1, 1, 1) \pm 3W^{(3)}(3; 2, 1) + W^{(3)}(3; 3) + 3W^{(3)}(2, 1; 3) \\ & \quad \pm 6W^{(3)}(2, 1; 1, 2) + W^{(3)}(1, 1, 1; 3)) + \dots \\ & \left. + \dots \right\}, \end{aligned} \quad (3.6)$$

where

$$d = N/\Omega, \quad v_0 = (h^2 \beta / 2\pi M)^{3/2},$$

$$\begin{aligned} W^{(2)}(2; 1, 1) &= \text{Tr } A^{(2)}(12) \delta^{(1)}(1) \delta^{(1)}(2), \\ W^{(2)}(2; 2) &= \text{Tr } A^{(2)}(12) \delta^{(2)}(12), \\ W^{(2)}(1, 1; 2) &= \text{Tr } A^{(1)}(1) A^{(1)}(2) \delta^{(2)}(12), \\ W^{(3)}(3; 1, 1, 1) &= \text{Tr } A^{(3)}(123) \delta^{(1)}(1) \delta^{(1)}(2) \delta^{(1)}(3), \\ W^{(3)}(3; 2, 1) &= \text{Tr } A^{(3)}(123) \delta^{(2)}(12) \delta^{(1)}(3), \\ W^{(3)}(3; 3) &= \text{Tr } A^{(3)}(123) \delta^{(3)}(123), \\ W^{(3)}(2, 1; 3) &= \text{Tr } A^{(2)}(12) A^{(1)}(3) \delta^{(3)}(123), \\ W^{(3)}(2, 1; 1, 2) &= \text{Tr } A^{(2)}(12) A^{(1)}(3) \delta^{(1)}(1) \delta^{(2)}(23), \\ W^{(3)}(1, 1, 1; 3) &= \text{Tr } A^{(1)}(1) A^{(1)}(2) A^{(1)}(3) \delta^{(3)}(123), \text{ etc.} \end{aligned} \quad (3.6')$$

and Ω is the volume of the imperfect gas. The numerical factor of each term is obtained by calculating the number of clusters W which are composed of operators A and operands δ . If the number N and the volume Ω tend to infinity under the condition that d is kept

constant, Eq. (3.6) becomes the asymptotic formula,

$$\exp(-\beta F) = \exp\left(-N \log(dv_0) - NdB - \frac{N}{2}d^2C - \dots\right), \quad (3.7)$$

$$B = -\frac{v_0^2}{2\Omega} \text{Tr} \{ \rho^{(2)}(12) \delta_{qu}^{(2)}(12) - \rho^{(1)}(1) \rho^{(1)}(2) \delta^{(1)}(1) \delta^{(1)}(2) \},$$

$$C = 4B^2 - 2B\Omega - \frac{v_0^3}{3\Omega} \text{Tr} \{ \rho^{(3)}(123) \delta_{qu}^{(3)}(123) - \rho^{(1)}(1) \rho^{(1)}(2) \rho^{(1)}(3) \delta^{(1)}(1) \delta^{(1)}(2) \delta^{(1)}(3) \}, \quad (3.8)$$

where

$$\delta_{qu}^{(2)}(12) = \delta^{(1)}(1) \delta^{(1)}(2) \pm \delta^{(2)}(12)$$

$$\delta_{qu}^{(3)}(123) = \delta^{(1)}(1) \delta^{(1)}(2) \delta^{(1)}(3) \pm (\delta^{(2)}(12) \delta^{(1)}(3) + \delta^{(2)}(23) \delta^{(1)}(1) + \delta^{(2)}(13) \delta^{(1)}(2)) + \delta^{(3)}(123). \quad (3.8')$$

In the above equation B and C are the 2nd and 3rd virial coefficient, respectively, because $p = -\partial F / \partial \Omega$. B is identical to the usual formula which appears in textbooks of statistical mechanics. If we do not spare any effort, the higher orders of virial coefficients are similarly obtained, but we can easily guess them. This is seen in Appendix B.

We shall now give the expansion formulas for the 2nd and 3rd virial coefficients in terms of $a^2 = \hbar^2 \beta / M$. These derivations are easily obtained by the calculus of the ordered exponential⁷⁾ and are applicable to the higher orders of virial coefficients. The mathematics is mentioned in Appendix C.

$$\begin{aligned} B &= B_{e1} + B_1 a^2 + B_2 a^4 + \dots, \\ C &= C_{e1} + C_1 a^2 + C_2 a^4 + \dots, \end{aligned} \quad (3.9)$$

If the potential is the function of relative co-ordinate $\mathbf{x}$ or $\mathbf{y}$, the coefficients of the above equation are determined as

$$\begin{aligned} B_{e1} &= -\frac{1}{2} \int d\mathbf{x} (e^{-\beta U} - 1), & B_1 &= \frac{\beta^2}{12} \frac{1}{2} \int d\mathbf{x} e^{-\beta U} (KU U), \\ B_2 &= \frac{\beta^2}{120} \frac{1}{2} \int d\mathbf{x} e^{-\beta U} \left\{ (KU(LU)) + \frac{\beta}{3} (KU(KUU)) - \frac{5\beta^2}{12} (KU U)^2 \right\}, \quad \text{etc.}, \end{aligned} \quad (3.10)$$

where the potential U and operators K and L are such that

$$U = V^{(2)}(\mathbf{x}), \quad (K\mathfrak{B}\mathfrak{B}) = \nabla_{\mathbf{x}} \mathfrak{B} \cdot \nabla_{\mathbf{x}} \mathfrak{B}, \quad (L\mathfrak{B}) = \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} \mathfrak{B} \quad (3.11)$$

where $\mathfrak{B}$ and $\mathfrak{B}$ are arbitrary functions. In the case of the 3rd virial coefficient we can similarly express them as

$$\begin{aligned} C_{e1} &= 4B_{e1}^2 - 2\Omega B_{e1} - \frac{1}{3} \iint d\mathbf{x} d\mathbf{y} (e^{-\beta U} - 1), \\ C_1 &= 8B_1 B_{e1} - 2\Omega B_1 + \frac{\beta^2}{12} \frac{1}{3} \iint d\mathbf{x} d\mathbf{y} e^{-\beta U} (KU U), \\ C_2 &= 4(2B_2 B_{e1} + B_1^2) - 2\Omega B_2 + \frac{\beta^2}{120} \frac{1}{3} \iint d\mathbf{x} d\mathbf{y} e^{-\beta U} \left\{ (KU(LU)) \right. \\ &\quad \left. + \frac{\beta}{3} (KU(KUU)) - \frac{5\beta^2}{12} (KU U)^2 \right\}, \quad \text{etc.}, \end{aligned} \quad (3.12)$$

where $\mathbf{x}$ and $\mathbf{y}$ are relative co-ordinates and U , K , and L are defined by

$$\begin{aligned}
 U &= V^{(2)}(\mathbf{x}) + V^{(2)}(\mathbf{y}) + V^{(2)}(\mathbf{x}-\mathbf{y}) + V^{(3)}(\mathbf{x}, \mathbf{y}), \\
 (K\mathfrak{B}\mathfrak{B}) &= \nabla_x \mathfrak{B} \cdot \nabla_x \mathfrak{B} + \nabla_y \mathfrak{B} \cdot \nabla_y \mathfrak{B} + \frac{1}{2} (\nabla_x \mathfrak{B} \cdot \nabla_y \mathfrak{B} + \nabla_y \mathfrak{B} \cdot \nabla_x \mathfrak{B}), \\
 (L\mathfrak{B}) &= \nabla_x \cdot \nabla_x \mathfrak{B} + \nabla_y \cdot \nabla_y \mathfrak{B} + \nabla_x \cdot \nabla_y \mathfrak{B}.
 \end{aligned} \tag{3.13}$$

The integrands in Eq. (3.12) are similar to those of Eq. (3.10). If the potential U , Laplacian L , and the kinetic energy tensor operator K are appropriately defined, these analogies will exist for the higher order virial coefficients and give us their expressions. C_1 in the above equation agrees with the result of Kihara, Mizuno and Shizume which was obtained by solving the Bloch equation.

§ 4. New Formulas for Multiple Scattering

If we make the Laplace transformation of the expansions of the density matrices, the formulas of multiple scattering are obtained. By making the Laplace transformation of Eq. (2.2) we obtain

$$\begin{aligned}
 \frac{1}{E-(H_0+V)} &= \frac{1}{E-H_0} + \sum_{\alpha} \frac{1}{E-H_0} T_{\alpha} \frac{1}{E-H_0} + \sum_{\alpha < \beta} \frac{1}{E-H_0} T_{\alpha\beta} \frac{1}{E-H_0} \\
 &+ \sum_{\alpha < \beta < \gamma} \frac{1}{E-H_0} T_{\alpha\beta\gamma} \frac{1}{E-H_0} + \cdots,
 \end{aligned} \tag{4.1}$$

where

$$\begin{aligned}
 V &= \sum_{\alpha} V_{\alpha}, \\
 T_{\alpha} &= V_{\alpha} \left(1 + \frac{1}{E-H_0} T_{\alpha} \right), \\
 T'_{\alpha\beta} &= (V_{\alpha} + V_{\beta}) \left(1 + \frac{1}{E-H_0} T'_{\alpha\beta} \right); \quad T_{\alpha\beta} = T'_{\alpha\beta} - T_{\alpha} - T_{\beta}, \\
 T'_{\alpha\beta\gamma} &= (V_{\alpha} + V_{\beta} + V_{\gamma}) \left(1 + \frac{1}{E-H_0} T'_{\alpha\beta\gamma} \right); \quad T_{\alpha\beta\gamma} = T'_{\alpha\beta\gamma} - T'_{\alpha\beta} - T'_{\beta\gamma} - T'_{\gamma\alpha} + T_{\alpha} + T_{\beta} + T_{\gamma}, \\
 &\text{etc.}
 \end{aligned} \tag{4.2}$$

The above formula agrees with that of Luttinger and Kohn.

If we make the Laplace transformation of Eq. (3.2) we obtain a new formula for multiple scattering:

$$\begin{aligned}
 \frac{1}{E-(H_0+V)} &= \frac{1}{E-H_0} + \sum_{i < j} \left\{ \frac{1}{E-H_0} t_{ij} \frac{1}{E-H_0} \right\} \\
 &+ \sum_{(i < j) \nleftrightarrow (k < l)} \left\{ \frac{1}{E-H_0} (M_{ij}^{kl} - t_{kl}) \frac{1}{E-H_0} + \frac{1}{E-H_0} (M_{kl}^{ij} - t_{ij}) \frac{1}{E-H_0} \right\} + \cdots \\
 &+ \sum_{i < j < k} \left\{ \frac{1}{E-H_0} v_{ijk} \frac{1}{E-H_0} \right\} + \cdots \\
 &+ \sum_{i < j < k < l} \left\{ \frac{1}{E-H_0} w_{ijkl} \frac{1}{E-H_0} \right\} + \cdots \\
 &+ \cdots \cdots \cdots
 \end{aligned} \tag{4.3}$$

where

$$\begin{aligned}
V &= \sum_{i < j} V_{ij}^{(2)} + \sum_{i < j < k} V_{ijk}^{(3)} + \cdots, \\
t_{ij} &= V_{ij}^{(2)} \left(1 + \frac{1}{E-H_0} t_{ij} \right), \quad M_{ij}^{kl} = t_{kl} \left(1 + \frac{1}{E-H_0} M_{kl}^{ij} \right), \\
v'_{ijk} &= (V_{ij}^{(2)} + V_{jk}^{(2)} + V_{kl}^{(2)} + V_{ijk}^{(3)}) \left(1 + \frac{1}{E-H_0} v'_{ijk} \right); \\
v_{ijk} &= v'_{ijk} - t_{ij} - t_{jk} - t_{kl}, \quad \text{etc.}, \\
w'_{ijkl} &= (V_{ij}^{(2)} + V_{jk}^{(2)} + V_{kl}^{(2)} + V_{li}^{(2)} + V_{ik}^{(2)} + V_{jl}^{(2)} + V_{ij}^{(3)} + V_{jkl}^{(3)} + V_{kli}^{(3)} + V_{lji}^{(3)} + V_{ilj}^{(3)} + V_{ijkl}^{(4)}) \\
&\quad \times \left(1 + \frac{1}{E-H_0} w'_{ijkl} \right) \\
w_{ijkl} &= w'_{ijkl} - M_{ij}^{kl} - M_{kl}^{ij} - M_{ik}^{jl} - M_{jl}^{ik} - M_{il}^{jk} - M_{jk}^{il} - v_{ijk} - v_{jkl} - v_{kli} - v_{lji}, \quad \text{etc.} \quad (4.4)
\end{aligned}$$

In the above equations t_{ij} represents a double collision, v_{ijk} a triple collision, w_{ijkl} a quartet collision, and M_{ij}^{kl} two double collisions. In these formulas Eq. (4.1) requires only $V = \sum_{\alpha} V_{\alpha}$ and Eq. (4.3) requires only $V = \sum_{i < j} V_{ij}^{(2)} + \sum_{i < j < k} V_{ijk}^{(3)} + \cdots$, being independent of the physical meaning of the V_{α} or the $V_{ij}^{(2)}$. Therefore when we apply these formulas to practical examples we need not restrict their application to collision problems.

§ 5. Normalization of the Density Matrix

In quantum statistical mechanics the expansion formula for the normalized density matrix is also important. In this section we shall discuss the expansion formula for the normalized density matrix. As is mentioned in Sections 2 and 3 the non-normalized density matrix ρ is expanded in such a way that

$$\rho = \rho^{(0)} + \sum_{\alpha} \rho_{\alpha}^{(1)} + \sum_{\alpha < \beta} \rho_{\alpha\beta}^{(2)} + \cdots \quad (5.1)$$

If we take the trace of the above equation, we obtain

$$\exp(-\beta F^{(0)}) (1 + \sum_{\alpha} I_{\alpha}^{(1)} + \sum_{\alpha < \beta} I_{\alpha\beta}^{(2)} + \cdots), \quad (5.2)$$

where $F^{(0)}$, $I_{\alpha}^{(1)}$, $I_{\alpha\beta}^{(2)}$, $\cdots$ are defined by the relations

$$\begin{aligned}
\exp(-\beta F^{(0)}) &= \text{Tr } \rho^{(0)}, \quad I_{\alpha}^{(1)} = \exp(\beta F^{(0)}) \text{Tr } \rho_{\alpha}^{(1)}, \\
I_{\alpha\beta}^{(2)} &= \exp(\beta F^{(0)}) \text{Tr } \rho_{\alpha\beta}^{(2)}, \quad \cdots
\end{aligned} \quad (5.3)$$

Using Eq. (5.2) the normalized density matrix $\exp(\beta F)\rho$ becomes

$$\exp(\beta F)\rho = \exp(\beta F^{(0)}) \frac{1}{1 + \sum_{\alpha} I_{\alpha}^{(1)} + \sum_{\alpha < \beta} I_{\alpha\beta}^{(2)} + \cdots} \rho. \quad (5.4)$$

We shall now discuss how to expand the denominator in Eq. (5.4). If the density matrix $\exp(-\beta(H_0 + \sum_{\alpha} V_{\alpha}^{(1)} + \sum_{\alpha < \beta} V_{\alpha\beta}^{(2)} + \cdots))$ is expanded in the same way as we have mentioned in Section 2, Eq. (5.1) becomes

$$\begin{aligned}
&\exp(-\beta(H_0 + \sum_{\alpha} V_{\alpha}^{(1)} + \sum_{\alpha < \beta} V_{\alpha\beta}^{(2)} + \cdots)) \\
&= \exp(-\beta H_0) + \sum_{\alpha} \{ \exp(-\beta(H_0 + V_{\alpha}^{(1)})) - \exp(-\beta H_0) \} \\
&\quad + \sum_{\alpha < \beta} \{ \exp(-\beta(H_0 + V_{\alpha}^{(1)} + V_{\beta}^{(1)} + V_{\alpha\beta}^{(2)})) - \exp(-\beta(H_0 + V_{\alpha}^{(1)})) \\
&\quad \quad - \exp(-\beta(H_0 + V_{\beta}^{(1)})) + \exp(-\beta H_0) \} \\
&\quad + \cdots
\end{aligned} \quad (5.5)$$

If we take the Laplace transformation of the above equation, we obtain a multiple scattering formula which is more general than Eqs. (4.1) and (4.3):

$$\begin{aligned} \frac{1}{E-(H_0+V)} = & \frac{1}{E-H_0} + \sum_{\alpha} \left\{ \frac{1}{E-(H_0+V_{\alpha}^{(1)})} - \frac{1}{E-H_0} \right\} \\ & + \sum_{\alpha < \beta} \left\{ \frac{1}{E-(H_0+V_{\alpha}^{(1)}+V_{\beta}^{(1)}+V_{\alpha\beta}^{(2)})} - \frac{1}{E-(H_0+V_{\alpha}^{(1)})} \right. \\ & \left. - \frac{1}{E-(H_0+V_{\beta}^{(1)})} + \frac{1}{E-H_0} \right\} \\ & + \cdots, \end{aligned} \quad (5.6)$$

where

$$V = \sum_{\alpha} V_{\alpha}^{(1)} + \sum_{\alpha < \beta} V_{\alpha\beta}^{(2)} + \cdots$$

As a particular case of the above theorem, the following relation is derived.

$$\begin{aligned} \frac{1}{1 + \sum_{\alpha} I_{\alpha}^{(1)} + \sum_{\alpha < \beta} I_{\alpha\beta}^{(2)} + \cdots} = & 1 + \sum_{\alpha} \left(\frac{1}{1 + I_{\alpha}^{(1)}} - 1 \right) \\ & + \sum_{\alpha < \beta} \left(\frac{1}{1 + I_{\alpha}^{(1)} + I_{\beta}^{(1)} + I_{\alpha\beta}^{(2)}} - \frac{1}{1 + I_{\alpha}^{(1)}} - \frac{1}{1 + I_{\beta}^{(1)}} + 1 \right) + \cdots \end{aligned} \quad (5.7)$$

If we put Eqs. (5.1) and (5.7) into Eq. (5.4) and rearrange it in the same manner as Eqs. (5.1) and (5.7) are expanded, we obtain

$$\exp(\beta F) = \exp(\beta F^{(0)}) \rho^{(0)} + \sum_{\alpha} \exp(\beta F^{(0)}) (\rho_{\alpha}^{(1)} - I_{\alpha}^{(1)} \rho^{(0)}) / (1 + I_{\alpha}^{(1)}) + \cdots, \quad (5.8)$$

which is our result. The formula obtained by the perturbation method is as follows.

$$\exp(\beta F) \rho = \exp(\beta F^{(0)}) \rho^{(0)} + \sum_{\alpha} \exp(\beta F^{(0)}) (\rho_{\alpha}^{(1)} - I_{\alpha}^{(1)} \rho^{(0)}) + \cdots \quad (5.9)$$

Eq. (5.9) is usually used, but is not correct unless $1 \gg I_{\alpha}^{(1)} \cdots$. Therefore the normalization of the density matrix should be chosen carefully.

§ 6. Formulas Applied to Irreversible Processes and Relaxation Phenomena

When we discuss irreversible processes and relaxation phenomena, we meet with the calculation of the following type,

$$\exp\left(\frac{it}{\hbar}(H_0 + V)\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V)\right)$$

or

$$\exp_{-}\left(\frac{i}{\hbar} \int_0^t ds V(s)\right) M(t) \exp_{+}\left(-\frac{i}{\hbar} \int_0^t ds V(s)\right). \quad (6.1)$$

In this section we shall show some formulas for the above operators expanded in the same way as was done in the previous sections. From the proof of the theorem in Section 2 we can see that the following relation holds:

$$\begin{aligned} \exp_{\pm}\left(\frac{i}{\hbar} \int_0^t ds V(s)\right) = & 1 + \sum_{\alpha} \left\{ \exp_{\pm}\left(\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)\right) - 1 \right\} \\ & + \sum_{\alpha < \beta} \left\{ \exp_{\pm}\left(\frac{i}{\hbar} \int_0^t ds (V_{\alpha}(s) + V_{\beta}(s))\right) - \exp_{\pm}\left(\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)\right) \right. \\ & \left. - \exp_{\pm}\left(\frac{i}{\hbar} \int_0^t ds V_{\beta}(s)\right) + 1 \right\} \\ & + \cdots, \end{aligned} \quad (6.2)$$

where

$$V(s) = \sum_{\alpha} V_{\alpha}(s) .$$

If we put Eq. (6.2) into Eq. (6.1), we obtain

$$\begin{aligned} \exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)\right) M(t) \exp\left(+\frac{i}{\hbar} \int_0^t ds V(s)\right) \\ = M(t) + \sum_{\alpha} \left\{ \exp\left(-\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)\right) M(t) \exp\left(+\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)\right) - M(t) \right\} + \dots \end{aligned} \quad (6.3)$$

In order to shorten the expression we introduce the following notation,

$$\begin{aligned} \exp\left(\frac{it}{\hbar}(H_0 + V)\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V)\right) &\equiv \exp\left(\frac{it}{\hbar}(H_0 + V)^{\times}\right) M , \\ \exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)\right) M(t) \exp\left(+\frac{i}{\hbar} \int_0^t ds V(s)\right) &\equiv \exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)^{\times}\right) M(t) . \end{aligned} \quad (6.4)$$

Eq. (6.3) then becomes

$$\begin{aligned} \exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)^{\times}\right) M(t) &= \left(1 + \sum_{\alpha} \left\{ \exp\left(-\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)^{\times}\right) - 1 \right\} \right. \\ &\quad + \sum_{\alpha < \beta} \left\{ \exp\left(-\frac{i}{\hbar} \int_0^t ds (V_{\alpha}(s) + V_{\beta}(s))^{\times}\right) - \exp\left(-\frac{i}{\hbar} \int_0^t ds V_{\alpha}(s)^{\times}\right) \right. \\ &\quad \left. \left. - \exp\left(-\frac{i}{\hbar} \int_0^t ds V_{\beta}(s)^{\times}\right) + 1 \right\} + \dots \right) M(t) . \end{aligned} \quad (6.5)$$

By comparing Eq. (6.4) with Eq. (6.2) we can see that the expansion of $\exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)^{\times}\right)$ is of the same form as $\exp\left(-\frac{i}{\hbar} \int_0^t ds V(s)\right)$. Similar circumstances hold for $\exp(it/\hbar \cdot (H + V)^{\times})$ and we can easily verify the following formulas which are particular cases of the theorem given in Appendix B.

Theorem. If $V = \sum_{i < j} V_{ij}^{(2)} + \sum_{i < j < k} V_{ijk}^{(3)} + \dots$, then

$$\begin{aligned} \exp\left(\frac{it}{\hbar}(H_0 + V)\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V)\right) \\ = \exp\left(\frac{it}{\hbar}H_0\right) M \exp\left(-\frac{it}{\hbar}H_0\right) + \sum_{i < j} \left\{ \exp\left(\frac{it}{\hbar}(H_0 + V_{ij}^{(2)})\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V_{ij}^{(2)})\right) \right. \\ \left. - \exp\left(\frac{it}{\hbar}H_0\right) M \exp\left(-\frac{it}{\hbar}H_0\right) \right\} + \dots \end{aligned} \quad (6.6)$$

If $V = \sum_{\alpha} V_{\alpha}^{(1)} + \sum_{\alpha < \beta} V_{\alpha\beta}^{(2)} + \dots$, then

$$\begin{aligned} \exp\left(\frac{it}{\hbar}(H_0 + V)\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V)\right) \\ = \exp\left(\frac{it}{\hbar}H_0\right) M \exp\left(-\frac{it}{\hbar}H_0\right) + \sum_{\alpha} \left\{ \exp\left(\frac{it}{\hbar}(H_0 + V_{\alpha}^{(1)})\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V_{\alpha}^{(1)})\right) \right. \\ \left. - \exp\left(\frac{it}{\hbar}H_0\right) M \exp\left(-\frac{it}{\hbar}H_0\right) \right\} + \dots \end{aligned} \quad (6.7)$$

In practical applications we sometimes meet the Laplace transformation of Eq. (6.1) which is given by the relation,

$$\begin{aligned}
 M(s) &= s \int_0^\infty dt \exp(-st) \exp\left(\frac{it}{\hbar}(H_0 + V)\right) M \exp\left(-\frac{it}{\hbar}(H_0 + V)\right) \\
 &= \frac{i\hbar s}{2\pi i} \int_{-\infty}^\infty dE \frac{1}{E - (H_0 + V) - i\hbar s/2} M \frac{1}{E - (H_0 + V) + i\hbar s/2}.
 \end{aligned} \quad (6.8)$$

If every term in Eqs. (6.6) and (6.7) is Laplace transformed by use of Eq. (6.8), the expansion theorems of the Laplace transformed formula are obtained.

We shall now give an example of the application of the formulas which have been mentioned in this section. The line shape $I(\omega)$ of the pressure broadening in a system consisting of one radiating atom and N perturbing atoms is given by the expression,⁹⁾

$$\begin{aligned}
 I(\omega) &= \frac{\beta}{2} \int_{-\infty}^\infty d\tau \exp(i\omega\tau) \Phi(\tau), \\
 \Phi(\tau) &= \text{Tr } \rho |M|^2 \exp\left(-\left(\frac{i}{\hbar} \int_0^\tau ds \exp\left(-\left(\frac{i}{\hbar} \int_0^s ds_1 V(s_1)\right) U(s) \exp_+\right) U(s) \exp_+\left(-\frac{i}{\hbar} \int_0^s ds_1 V(s_1)\right)\right)\right),
 \end{aligned} \quad (6.9)$$

where

$$\begin{aligned}
 U(s) &= \sum_j \{V_g(\mathbf{r}_{j0} + \mathbf{v}_{j0}s) - V_e(\mathbf{r}_{j0} + \mathbf{v}_{j0}s)\} \equiv \sum_j U(\mathbf{r}_{j0} + \mathbf{v}_{j0}s), \\
 V(s) &= \sum_{i < j} V'(\mathbf{r}_{ij} + \mathbf{v}_{ij}s) + \sum_j V_g(\mathbf{r}_{j0} + \mathbf{v}_{j0}s).
 \end{aligned} \quad (6.10)$$

The summation in Eq. (6.10) runs over all perturbors, and $\mathbf{r}_{j0}$ and $\mathbf{r}_{ij}$ are the relative coordinates between the j -th perturber and the radiating atom and between the i -th and the j -th perturbors, respectively. $\mathbf{v}_{j0}$ and $\mathbf{v}_{ij}$ are their relative velocity. V_g is the interaction potential between a perturber and the ground state of the radiating atom, V_e the interaction potential between a perturber and the radiating atom in the excited state and V' the interaction potential between two perturbors. Using Eq. (6.6) the integrand of $\frac{i}{\hbar} \int_0^\tau ds$ in Eq. (6.9) becomes

$$\begin{aligned}
 &\exp\left(-\left(\frac{i}{\hbar} \int_0^s ds_1 V(s_1)\right) U(s) \exp_+\left(-\frac{i}{\hbar} \int_0^s ds_1 V(s_1)\right)\right) \\
 &= \sum_j \left\{ \exp\left(\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{j0}))\right) U(\mathbf{r}_{j0}) \exp\left(-\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{j0}))\right) \right\} \\
 &\quad + \sum_{i < j} \left\{ \exp\left(\frac{is}{\hbar}(H_0 + V'(\mathbf{r}_{ij}) + V_g(\mathbf{r}_{i0}) + V_g(\mathbf{r}_{j0}))\right) (U(\mathbf{r}_{i0}) + U(\mathbf{r}_{j0})) \right. \\
 &\quad \times \exp\left(-\frac{is}{\hbar}(H_0 + V'(\mathbf{r}_{ij}) + V_g(\mathbf{r}_{i0}) + V_g(\mathbf{r}_{j0}))\right) \\
 &\quad - \exp\left(\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{i0}))\right) U(\mathbf{r}_{i0}) \exp\left(-\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{i0}))\right) \\
 &\quad \left. - \exp\left(\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{j0}))\right) U(\mathbf{r}_{j0}) \exp\left(-\frac{is}{\hbar}(H_0 + V_g(\mathbf{r}_{j0}))\right) \right\} + \dots.
 \end{aligned} \quad (6.11)$$

The 1st term represents the effect of collision between one perturber and the radiating atom, and the 2nd term represents the effect of collisions between two perturbors and the radiating atom, which originates from V' being non-zero; namely, this is an effect of the curving of the path of one perturber by the others and may be an important correction at high density.

§ 7. Concluding Remarks and Acknowledgements

The formulas which are derived in this paper are important in quantum statistical mecha-

tics, and are useful when we discuss the scattering problems and the kinetic theory of dissipative systems in terms of the expansion of the concentration. These are mathematically correct but correct results are not derived unless they are correctly applied.

In most cases which appear in physics, the correction terms at high density should be zero when the constituent elements are separated to infinity. For instance double collision should be zero in the interaction representation when colliding particles are infinitely separate. Indeed this requirement is satisfied when the interaction potential $V^{(2)}$ of the two particles vanishes at infinite separation. In the case of this type of potential, if the formulas (3.2), (4.3) and (6.6) are applied, correct results are obtained, but in Eqs. (2.2) and (4.2) the higher terms of the expansion do not always vanish when constituent elements are separated to infinite distance. For example, consider the 3rd term of the expansion of Eq. (2.2),

$$\{\exp(-\beta(H_0 + V_\alpha + V_\beta)) - \exp(-\beta(H_0 + V_\alpha)) - \exp(-\beta(H_0 + V_\beta)) + \exp(-\beta H_0)\}.$$

This vanishes only if V_α and V_β are simultaneously zero and is not always zero even if α β are infinite distant. Similar circumstances exist in Eqs. (5.5), (5.6) and (6.7). Therefore when we use these formulas physical consideration should be taken carefully. Other applications of these formula will be postponed in subsequent papers.

The author wishes to express his sincere thanks to Professor R. Kubo of the University of Tokyo who has had the kindness to lead the author. The present study was partially financed by the Scientific Research Fund of the Ministry of Education.

Appendix A. Expansion Formula for $\delta_{qu}^{(n)}$

The expansion formula for $\delta_{qu}^{(N)}$, Eq. (3.5) is derived by Ursell's theorem which is as follows

$$\begin{aligned} \delta_{qu}^{(1)}(1) &= \delta^{(1)}(1), & \delta_{qu}^{(2)}(12) &= \delta^{(1)}(1)\delta^{(1)}(2) + \delta_{\pm}^{(2)}(12), \\ \delta_{qu}^{(3)}(123) &= \delta^{(1)}(1)\delta^{(1)}(2)\delta^{(1)}(3) + \delta^{(1)}(1)\delta_{\pm}^{(2)}(23) + \delta^{(1)}(2)\delta_{\pm}^{(2)}(13) + \delta^{(1)}(3)\delta_{\pm}^{(2)}(12) + \delta_{\pm}^{(3)}(123), \\ &\dots\dots\dots \\ \delta_{qu}^{(N)}(12\dots N) &= \prod_{h=1}^N \delta^{(1)}(h) + \sum_{i < j} \delta_{\pm}^{(2)}(ij) \prod_{j \neq i, j} \delta^{(1)}(h) + \dots \end{aligned} \quad (\text{A.1})$$

Remembering that

$$\begin{aligned} \delta_{qu}^{(1)}(1) &= \delta(\mathbf{x}_1 - \mathbf{x}_1'), & \delta_{qu}^{(2)}(12) &= \delta(\mathbf{x}_1 - \mathbf{x}_1')\delta(\mathbf{x}_2 - \mathbf{x}_2') \pm \delta(\mathbf{x}_1 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_1'), \\ \delta_{qu}^{(3)}(123) &= \begin{vmatrix} \delta(\mathbf{x}_1 - \mathbf{x}_1') & \delta(\mathbf{x}_1 - \mathbf{x}_2') & \delta(\mathbf{x}_1 - \mathbf{x}_3') \\ \delta(\mathbf{x}_2 - \mathbf{x}_1') & \delta(\mathbf{x}_2 - \mathbf{x}_2') & \delta(\mathbf{x}_2 - \mathbf{x}_3') \\ \delta(\mathbf{x}_3 - \mathbf{x}_1') & \delta(\mathbf{x}_3 - \mathbf{x}_2') & \delta(\mathbf{x}_3 - \mathbf{x}_3') \end{vmatrix}_{\pm}, & \text{etc.}, \end{aligned} \quad (\text{A.2})$$

and solving Eq. (A.1) for $\delta_{\pm}^{(2)}(12)$, $\dots$ and $\delta_{\pm}^{(N)}(12\dots N)$ we obtain

$$\delta_{\pm}^{(2)}(12) = \pm \delta^{(2)}(12), \quad \delta_{\pm}^{(3)}(123) = \delta^{(3)}(123), \quad \delta_{\pm}^{(4)}(1234) = \pm \delta^{(4)}(1234), \quad \text{etc.}, \quad (\text{A.3})$$

where $\delta^{(2)}(12)$ and $\delta^{(3)}(123)$ are defined by Eq. (3.5') and

$$\begin{aligned} \delta^{(4)}(1234) &= \delta(\mathbf{x}_1 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_1') + \delta(\mathbf{x}_1 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_1') \\ &\quad + \delta(\mathbf{x}_1 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_1') + \delta(\mathbf{x}_1 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_1') \\ &\quad + \delta(\mathbf{x}_1 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_1') + \delta(\mathbf{x}_1 - \mathbf{x}_4')\delta(\mathbf{x}_4 - \mathbf{x}_3')\delta(\mathbf{x}_3 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_1') \\ &= \sum_{6 \text{ terms}} P \delta(\mathbf{x}_1 - \mathbf{x}_i')\delta(\mathbf{x}_i - \mathbf{x}_j')\delta(\mathbf{x}_j - \mathbf{x}_k')\delta(\mathbf{x}_k - \mathbf{x}_1'). \end{aligned} \quad (\text{A.4})$$

The general term $\delta_{\pm}^{(n)}(12\dots n)$ is $(\pm)^{(n-1)}\delta^{(n)}(12\dots n)$ where $\delta^{(n)}(12\dots n)$ consists of $(n-1)!$ terms. Each of them is such a product of n δ -functions that, if each of these δ -functions $\delta(\mathbf{x}_i - \mathbf{x}_j')$ corresponds to a stick having the i -th bolt at one terminal and the j -th nut at the

other terminal, and the bolt and nut which have the same numbering are fastened, then a ring is made of n sticks.

Appendix B. Higher Order Virial Coefficients

If we put Eqs. (3.2) and (3.5) into Eq. (3.3) and rearrange it in the same way as Eq. (3.2), we obtain

$$\begin{aligned} \frac{1}{N!} \text{Tr } e^{-\beta(H_0+V)} \delta_{qu}^{(N)} &= e^{-\beta F} \\ &= \frac{\mathcal{Q}^N}{N! v_0^N} \left\{ 1 + \sum_{i < j} \frac{v_0^2}{\mathcal{Q}^2} \text{Tr } B^{(2)}(ij) + \sum_{(i < j) \neq (k < l)} \frac{v_0^4}{\mathcal{Q}^4} \text{Tr } B^{(2)}(ij) B^{(2)}(kl) + \cdots \right. \\ &\quad \left. + \sum_{i < j < k} \frac{v_0^3}{\mathcal{Q}^3} \text{Tr } B^{(3)}(ijk) + \cdots + \sum_{i < j < k < l} \frac{v_0^4}{\mathcal{Q}^4} \text{Tr } B^{(4)}(ijkl) + \cdots \right\}, \end{aligned} \quad (\text{B.1})$$

where the functions indicated by B are determined by the combinations of operators A and operands δ . If the cluster integrals $b_2, b_3, b_4, \dots$ are defined by

$$\begin{aligned} b_2 &= \frac{v_0^2}{2! \mathcal{Q}} \text{Tr } B^{(2)}(ij), \quad b_3 = \frac{v_0^3}{3! \mathcal{Q}} \text{Tr } B^{(3)}(ijk), \quad b_4 = \frac{v_0^4}{4! \mathcal{Q}} \text{Tr } B^{(4)}(ijkl), \\ &\dots \dots b_n = \frac{v_0^n}{n! \mathcal{Q}} \text{Tr } B^{(n)}(12 \cdots n), \dots \dots \end{aligned} \quad (\text{B.2})$$

then Eq. (B.1) becomes the similar expression as Mayer's classical expression. Therefore Mayer's mathematics is applied to this case and the virial coefficients are given as follows:

$$B = -b_2, \quad C = 4B^2 - 2b_3, \quad D = 12BC - 12B^3 - 3b_4, \quad \text{etc.}, \quad (\text{B.3})$$

where D is the 4th virial coefficient. In order to calculate virial coefficients we must obtain expressions for the functions B in Eq. (B.1). This is easily done by the following theorem:

Theorem If there exist the two series $F^{(N)}$ and $G^{(N)}$ which are expanded in the same way as Eq. (3.2) i.e.,

$$\begin{aligned} F^{(N)} &= \prod_{h=1}^N f^{(1)}(h) + \sum_{i < j} f^{(2)}(ij) \prod_{h \neq i, j} f^{(1)}(h) + \sum_{(i < j) \neq (k < l)} f^{(2)}(ij) f^{(2)}(kl) \prod_{h \neq i, j, k, l} f^{(1)}(h) + \cdots \\ &\quad + \sum_{i < j < k} f^{(3)}(ijk) \prod_{h \neq i, j, k} f^{(1)}(h) + \cdots, \\ G^{(N)} &= \prod_{h=1}^N g^{(1)}(h) + \sum_{i < j} g^{(2)}(ij) \prod_{h \neq i, j} g^{(1)}(h) + \sum_{(i < j) \neq (k < l)} g^{(2)}(ij) g^{(2)}(kl) \prod_{h \neq i, j, k, l} g^{(1)}(h) + \cdots \\ &\quad + \sum_{i < j < k} g^{(3)}(ijk) \prod_{h \neq i, j, k} g^{(1)}(h) + \cdots, \end{aligned} \quad (\text{B.5})$$

and if the product $F^{(N)} G^{(N)}$ of these series is rearranged in the same manner as the above expansion, i.e.,

$$\begin{aligned} F^{(N)} G^{(N)} &= \prod_{h=1}^N P^{(1)}(h) + \sum_{i < j} P^{(2)}(ij) \prod_{h \neq i, j} P^{(1)}(h) + \sum_{(i < j) \neq (k < l)} P^{(2)}(ij) P^{(2)}(kl) \prod_{h \neq i, j, k, l} P^{(1)}(h) + \cdots \\ &\quad + \sum_{i < j < k} P^{(3)}(ijk) \prod_{h \neq i, j, k} P^{(1)}(h) + \cdots, \end{aligned} \quad (\text{B.6})$$

then the functions P are determined by the relations

$$\begin{aligned} F^{(1)}(i) G^{(1)}(i) &= P^{(1)}(i), \quad F^{(2)}(ij) G^{(2)}(ij) = P^{(1)}(i) P^{(1)}(j) + P^{(2)}(ij), \\ F^{(3)}(ijk) G^{(3)}(ijk) &= P^{(1)}(i) P^{(1)}(j) P^{(1)}(k) + P^{(1)}(i) P^{(2)}(jk) + P^{(1)}(j) P^{(2)}(ik) + P^{(1)}(k) P^{(2)}(ij) + P^{(3)}(ijk), \\ &\quad \text{etc.} \end{aligned} \quad (\text{B.7})$$

This is easily seen from the facts that the f 's, g 's and P 's are defined by Ursell's theorem.

If Eq. (B.7) is solved for functions P , and then F , G and P are replaced by ρ_{qu} , δ and B , respectively, we obtain

$$\begin{aligned}
 B^{(1)}(i) &= \rho^{(1)}(i) \delta^{(1)}(i), & B^{(2)}(ij) &= \rho^{(2)}(ij) \delta_{qu}^{(2)}(ij) - \rho^{(1)}(i) \rho^{(1)}(j) \delta^{(1)}(i) \delta^{(1)}(j), \\
 B^{(3)}(ijk) &= \rho^{(3)}(ijk) \delta_{qu}^{(3)}(ijk) - \sum_{3 \text{ terms}} P \rho^{(1)}(i) \rho^{(2)}(jk) \delta^{(1)}(i) \delta^{(2)}(jk) \\
 &\quad + 2 \rho^{(1)}(i) \rho^{(1)}(j) \rho^{(1)}(k) \delta^{(1)}(i) \delta^{(1)}(j) \delta^{(1)}(k), \\
 B^{(4)}(ijkl) &= \rho^{(4)}(ijkl) \delta_{qu}^{(4)}(ijkl) - \sum_{4 \text{ terms}} P \rho^{(1)}(i) \rho^{(3)}(jkl) \delta^{(1)}(i) \delta_{qu}^{(3)}(jkl) \\
 &\quad - \sum_{3 \text{ terms}} P \rho^{(2)}(ij) \rho^{(2)}(kl) \delta_{qu}^{(2)}(ij) \delta_{qu}^{(2)}(kl) \\
 &\quad + 2 \sum_{6 \text{ terms}} P \rho^{(1)}(i) \rho^{(1)}(j) \rho^{(2)}(kl) \delta^{(1)}(i) \delta^{(1)}(j) \delta_{qu}^{(2)}(kl) - 6 \prod_{h=i,j,k,l} \rho^{(1)}(h) \delta^{(1)}(h). \quad (B.8)
 \end{aligned}$$

The above formulas are easily derived with the aid of the analogy to Eq. (3.2') which is well known formula.

Using Eqs. (B.2), (B.3) and (B.8) the virial coefficients are calculated. The 2nd and 3rd virial coefficients B , C which are obtained by this method agree with Eq. (3.8) and the 4th virial coefficient D is given by

$$D = 12BC - 12B^3 - 18\mathcal{Q}^2C - 18\mathcal{Q}^2B + 90\mathcal{Q}B^2 - \frac{3v_0^4}{2\mathcal{Q}} \text{Tr} \left(\rho^{(4)}(1234) \delta_{qu}^{(4)}(1234) - \prod_{h=1}^4 \rho^{(1)}(h) \delta^{(1)}(h) \right). \quad (B.9)$$

These formulas of B , C and D are useful to calculate the numerical values of those virial coefficients. They are important particularly to get the values at low temperatures. From Eq. (B.8) we can see the fact that if the numerical values of the 2nd, the 3rd, $\dots$ and the n -th virial coefficients are known, then the $(n+1)$ -th virial coefficient is obtained by calculating numerically only the following expression,

$$\text{Tr} \left(\rho^{(n+1)}(12 \dots n+1) \delta_{qu}^{(n+1)}(12 \dots n+1) - \prod_{h=1}^{n+1} \rho^{(1)}(h) \delta^{(1)}(h) \right). \quad (B.10)$$

On the basis of this fact we shall discuss in Appendix C the expansion formula for the virial coefficient at high temperature.

Appendix C. Expansion Formula in Terms of $\hbar^2\beta/M$

We shall expand Eq. (3.8) in a power series of $\hbar^2\beta/M$ by the calculus of the ordered exponential. We shall introduce the following new variables instead of the co-ordinates r_i of the i -th molecule.

$$r_1 + r_2 + r_3 = 3R, \quad r_1 - r_3 = x, \quad r_2 - r_3 = y. \quad (C.1)$$

The Laplacian with respect to the new variables becomes

$$\begin{aligned}
 \frac{\partial}{\partial r_1} \cdot \frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} \cdot \frac{\partial}{\partial r_2} + \frac{\partial}{\partial r_3} \cdot \frac{\partial}{\partial r_3} &= \frac{1}{3} \frac{\partial}{\partial R} \cdot \frac{\partial}{\partial R} + 2 \frac{\partial}{\partial x} \cdot \frac{\partial}{\partial x} + 2 \frac{\partial}{\partial y} \cdot \frac{\partial}{\partial y} + 2 \frac{\partial}{\partial x} \cdot \frac{\partial}{\partial y} \\
 &= \frac{1}{3} \frac{\partial}{\partial R} \cdot \frac{\partial}{\partial R} + 2L. \quad (C.2)
 \end{aligned}$$

If the δ -functions are expressed by Fourier integrals and the integration with respect to R is performed, then Eq. (3.8) becomes as follows;

$$C=4B^2-2\mathcal{Q}B+\frac{1}{3}\mathcal{Q}^2 -\frac{v_0^2}{3}\frac{3^{3/2}}{(2\pi)^6}\int d\mathbf{x}\int d\mathbf{Y}\int\int d\mathbf{x}d\mathbf{y}(\exp(-i\mathbf{X}\cdot\mathbf{x}-i\mathbf{Y}\cdot\mathbf{y})\pm 3\exp(-i\mathbf{X}\cdot(\mathbf{x}+\mathbf{y})+i\mathbf{Y}\cdot\mathbf{y}) +2\exp(i\mathbf{X}\cdot(\mathbf{x}+\mathbf{y})+i\mathbf{Y}\cdot\mathbf{x}))\exp\left(-\beta\left(-\frac{\hbar^2}{M}L+U(\mathbf{x},\mathbf{y})\right)\right)\exp(i(\mathbf{X}\cdot\mathbf{x}+\mathbf{Y}\cdot\mathbf{y})), \quad (C.3)$$

where

$$U(\mathbf{x}, \mathbf{y})=V^{(2)}(\mathbf{x})+V^{(2)}(\mathbf{y})+V^{(2)}(\mathbf{x}-\mathbf{y})+V^{(3)}(\mathbf{x}, \mathbf{y}).$$

The terms $\pm 3\exp(-i\mathbf{X}\cdot(\mathbf{x}+\mathbf{y})+i\mathbf{Y}\cdot\mathbf{y})+2\exp(i\mathbf{X}\cdot(\mathbf{x}+\mathbf{y})+i\mathbf{Y}\cdot\mathbf{x})$ in the above equation come from the symmetry of Eq. (3.4) and their contribution is negligibly small at high temperatures. Therefore we shall omit them. In Eq. (C.3) the transformation of $\exp(i\mathbf{X}\cdot\mathbf{x}+i\mathbf{Y}\cdot\mathbf{y})$ is easily performed and the integrand in Eq. (C.3) becomes

$$\exp\left(-\frac{\beta\hbar^2}{M}(\mathbf{X}^2+\mathbf{Y}^2+\mathbf{X}\cdot\mathbf{Y})\right)\exp\left(\frac{\hbar^2\beta}{M}L-\beta U(\mathbf{x}, \mathbf{y})+\frac{\hbar^2\beta i}{M}\mathfrak{D}\right)1, \quad (C.4)$$

where

$$\mathfrak{D}=(2\mathbf{X}+\mathbf{Y})\cdot\boldsymbol{\nabla}_x+(\mathbf{X}+2\mathbf{Y})\cdot\boldsymbol{\nabla}_y.$$

In the above equation if the factor $\exp(\hbar^2\beta/M\cdot i\mathfrak{D})$ is separated to the right by use of the calculus of ordered exponentials, and new variables $\mathbf{X}$ and $\mathbf{Y}$ are introduced for $\sqrt{\beta\hbar^2/M}\mathbf{X}$ and $\sqrt{\beta\hbar^2/M}\mathbf{Y}$, respectively, then Eq. (C.3) becomes

$$C=4B^2-2\mathcal{Q}B+\frac{1}{3}\mathcal{Q}^2-\frac{1}{3}\frac{3^{3/2}}{(2\pi)^3}\int\int d\mathbf{x}d\mathbf{y}\int d\mathbf{X}\int d\mathbf{Y}\exp(-(X^2+Y^2+\mathbf{X}\cdot\mathbf{Y})) \times \exp_+\left(\int_0^1 ds(a^2L-\beta U(\mathbf{x}, \mathbf{y}, s))\right)1, \quad (C.5)$$

where

$$a^2=\hbar^2\beta/M,$$

$$U(\mathbf{x}, \mathbf{y}, s)=U(\mathbf{x}+i(1-s)a(2\mathbf{X}+\mathbf{Y}), \mathbf{y}+i(1-s)a(2\mathbf{Y}+\mathbf{X}))=\sum_{n=0}^{\infty}\frac{(ia(1-s))^n}{n!}\mathfrak{D}^n U(\mathbf{x}, \mathbf{y}).$$

If we further separate the factor $\exp_+\left(-\beta\int_0^1 ds U(\mathbf{x}, \mathbf{y}, s)\right)$ to the left, the ordered exponential in Eq. (C.5) becomes as follows:

$$\begin{aligned} &\exp_+\left(\int_0^1 ds(a^2L-\beta U(\mathbf{x}, \mathbf{y}, s))\right) \\ &=\exp\left(-\beta\int_0^1 ds U(\mathbf{x}, \mathbf{y}, s)\right)\exp_+\left(\int_0^1 ds\left\{a^2L-2\beta a^2K\int_0^s ds'U(\mathbf{x}, \mathbf{y}, s') \right. \right. \\ &\quad \left. \left. +\beta^2a^2\left(K\int_0^s ds'U(\mathbf{x}, \mathbf{y}, s')\int_0^s ds''U(\mathbf{x}, \mathbf{y}, s'')\right)-\beta a^2\left(L\int_0^s ds'U(\mathbf{x}, \mathbf{y}, s')\right)\right\}\right) \end{aligned} \quad (C.6)$$

where K and L are operators which are defined by Eq. (3.13).

Eq. (C.6) is most convenient to obtain the expansion formula in $\hbar^2\beta/M$, since if the ordered exponential is expanded, the power series in a^2 is obtained. As it contains the parameter a , the factor $\exp\left(-\beta\int_0^1 ds U(\mathbf{x}, \mathbf{y}, s)\right)$ ought to be also expanded in the power series of a . This calculation is, however, not so cumbersome, because we can neglect odd powers of $\mathfrak{D}$ which become zero when the integration of $\mathbf{X}$ and $\mathbf{Y}$ are performed in Eq. (C.5). In these calculations we must pay attention to the fact that the first two terms in

the ordered exponential and $\mathfrak{D}$ are operators which operate on the whole factors situated to the right of their operators when the exponentials are formally expanded. By the above, Eq. (C.6) becomes as follows:

$$\begin{aligned} \exp(-\beta U(\mathbf{x}, \mathbf{y})) & \left[1 + a^2 \left(\frac{\beta}{6} (\mathfrak{D}^2 U) - \frac{\beta^2}{8} (\mathfrak{D} U)^2 \right) + a^4 \left(-\frac{\beta}{120} (\mathfrak{D}^4 U) + \frac{\beta^2}{48} (\mathfrak{D} U)(\mathfrak{D}^3 U) \right. \right. \\ & \quad \left. \left. + \frac{\beta^2}{72} (\mathfrak{D}^2 U)^2 - \frac{\beta^3}{48} (\mathfrak{D} U)^2 (\mathfrak{D}^2 U) + \frac{\beta^4}{384} (\mathfrak{D} U)^4 \right) \right. \\ & \quad \left. + a^2 \left(\frac{\beta^2}{3} (KUU) - \frac{\beta}{2} (LU) \right) \right. \\ & \quad \left. + a^4 \left(\frac{3}{8} (L(\mathfrak{D}^2 U)) - \frac{\beta}{6} (L(LU)) - \frac{3\beta^2}{20} (KU(\mathfrak{D}^2 U)) - \frac{2\beta^2}{15} (K(\mathfrak{D} U)(\mathfrak{D} U)) \right. \right. \\ & \quad \left. \left. + \frac{\beta^2}{12} (L(KUU)) + \frac{\beta^2}{4} (KU(LU)) + \frac{\beta^2}{8} (LU)^2 - \frac{\beta^2}{6} (\mathfrak{D} U)(L(\mathfrak{D} U)) - \frac{\beta^2}{12} (\mathfrak{D}^2 U)(LU) \right. \right. \\ & \quad \left. \left. - \frac{2\beta^3}{15} (KU(KUU)) - \frac{\beta^3}{6} (LU)(KUU) + \frac{5\beta^3}{24} (\mathfrak{D} U)(KU(\mathfrak{D} U)) + \frac{\beta^3}{18} (\mathfrak{D}^2 U)(KUU) \right. \right. \\ & \quad \left. \left. + \frac{\beta^3}{16} (\mathfrak{D} U)^2 (LU) + \frac{\beta^4}{18} (KUU)^2 - \frac{\beta^4}{24} (\mathfrak{D} U)^2 (KUU) \right) + \dots \right]. \quad (\text{C.7}) \end{aligned}$$

If we replace the ordered exponential in Eq. (C. 5) by Eq. (C. 7) and partially integrate by $\mathbf{x}$ and $\mathbf{y}$, Eq. (C. 7) becomes simpler, that is,

$$\begin{aligned} \exp(-\beta U(\mathbf{x}, \mathbf{y})) & \left[1 + a^2 \beta^2 \left(\frac{1}{24} (\mathfrak{D} U)^2 - \frac{1}{6} (KUU) \right) \right. \\ & \quad \left. + a^4 \left\{ -\frac{\beta^2}{720} (\mathfrak{D}^3 U)(\mathfrak{D} U) + \frac{\beta^4}{3456} (\mathfrak{D} U)^4 + \frac{\beta^2}{40} (KU(\mathfrak{D}^2 U)) - \frac{\beta^2}{24} (KU(LU)) \right. \right. \\ & \quad \left. \left. - \frac{\beta^3}{120} (KU(KUU)) + \frac{\beta^3}{180} (\mathfrak{D} U)(KU(\mathfrak{D} U)) + \frac{\beta^4}{72} (KUU)^2 - \frac{\beta^4}{144} (\mathfrak{D} U)^2 (KUU) \right\} \right. \\ & \quad \left. + \dots \right]. \quad (\text{C.8}) \end{aligned}$$

Eqs. (C.7) and (C.8) are derived in the case of the 3rd virial coefficient. These relations are also used to get the expansion of the 2nd virial coefficient, because at high temperature the 2nd virial coefficient is given by the relation

$$\begin{aligned} B &= \frac{1}{2} \Omega - \frac{1}{2} \frac{2^{3/2}}{(2\pi)^{3/2}} \int d\mathbf{x} \int d\mathbf{X} \exp(-\mathbf{X}^2) \exp(a^2 \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} - \beta V^{(2)}(\mathbf{x}) + 2a i \mathbf{X} \cdot \nabla_{\mathbf{x}}) 1 \\ &= \frac{1}{2} \Omega - \frac{1}{2} \frac{2^{3/2}}{(2\pi)^{3/2}} \int d\mathbf{x} \int d\mathbf{X} \exp(-\mathbf{X}^2) \exp_+ \left(\int_0^1 ds (a^2 \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} - \beta V^{(2)}(\mathbf{x} + i(1-s)2a\mathbf{X})) \right) 1. \quad (\text{C.9}) \end{aligned}$$

In the case of the 2nd virial coefficient if the operators $\mathfrak{D}$, K , L and potential U are defined by the relations,

$$\mathfrak{D} = 2\mathbf{X} \cdot \nabla_{\mathbf{x}}, \quad K = \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}}, \quad L = \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}}, \quad U = V^{(2)}(\mathbf{x}), \quad (\text{C.10})$$

instead of the relations which are used in the case of the 3rd virial coefficient,

$$\begin{aligned} \mathfrak{D} &= (2\mathbf{X} + \mathbf{Y}) \cdot \nabla_{\mathbf{x}} + (2\mathbf{Y} + \mathbf{X}) \cdot \nabla_{\mathbf{y}}, & K &= \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} + \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{y}} + \frac{1}{2} (\nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{y}} + \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{x}}), \\ L &= \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{x}} + \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{y}} + \nabla_{\mathbf{x}} \cdot \nabla_{\mathbf{y}}, & U &= V^{(2)}(\mathbf{x}) + V^{(2)}(\mathbf{y}) + V^{(2)}(\mathbf{x} - \mathbf{y}) + V^{(3)}(\mathbf{x}, \mathbf{y}), \quad (\text{C.11}) \end{aligned}$$

then there are the same circumstances as in the case of the 3rd virial coefficient, and Eqs. (C.7) and (C.8) hold.

Now if we perform the integration with respect to $\mathbf{X}$ or $\mathbf{X}$ and $\mathbf{Y}$, we obtain similar relations for both the 2nd and 3rd virial coefficients.

$$\begin{aligned} \frac{2^{3/2}}{(2\pi)^{3/2}} \int d\mathbf{X} \exp(-\mathbf{X}^2) &= 1 = \frac{3^{3/2}}{(2\pi)^{3/2}} \iint d\mathbf{X} d\mathbf{Y} \exp(-\mathbf{X}^2 - \mathbf{Y}^2 - \mathbf{X} \cdot \mathbf{Y}), \\ \frac{2^{3/2}}{(2\pi)^{3/2}} \int d\mathbf{X} \exp(-\mathbf{X}^2) \mathfrak{B} \mathfrak{B} \mathfrak{B} &= 2(K \mathfrak{B} \mathfrak{B}) = \frac{3^{3/2}}{(2\pi)^{3/2}} \iint d\mathbf{X} d\mathbf{Y} \exp(-\mathbf{X}^2 - \mathbf{Y}^2 - \mathbf{X} \cdot \mathbf{Y}) \mathfrak{B} \mathfrak{B} \mathfrak{B}, \\ \frac{2^{3/2}}{(2\pi)^{3/2}} \int d\mathbf{X} \exp(-\mathbf{X}^2) \mathfrak{B}_1 \mathfrak{B}_2 \mathfrak{B}_3 \mathfrak{B}_4 & \\ &= 4\{(K \mathfrak{B}_1 \mathfrak{B}_2)(K \mathfrak{B}_3 \mathfrak{B}_4) + (K \mathfrak{B}_1 \mathfrak{B}_3)(K \mathfrak{B}_2 \mathfrak{B}_4) + (K \mathfrak{B}_1 \mathfrak{B}_4)(K \mathfrak{B}_2 \mathfrak{B}_3)\} \\ &= \frac{3^{3/2}}{(2\pi)^{3/2}} \iint d\mathbf{X} d\mathbf{Y} \exp(-\mathbf{X}^2 - \mathbf{Y}^2 - \mathbf{X} \cdot \mathbf{Y}) \mathfrak{B}_1 \mathfrak{B}_2 \mathfrak{B}_3 \mathfrak{B}_4, \quad \text{etc.} \end{aligned} \quad (\text{C.12})$$

Using Eq. (C.12), the integrations of Eqs. (C.5) and (C.9) become

$$-\frac{1}{n} \int \exp(-\beta U) \left\{ 1 - a^2 \beta^2 \frac{1}{12} (KUU) + \frac{a^4 \beta^2}{120} \left(-(KU(LU)) - \frac{\beta}{3} (KU(KUU)) + \frac{5\beta^2}{12} (KUU)^2 \right) + \dots \right\} \quad (\text{C.13})$$

where $n=2$, and the variables of integration are $d\mathbf{x}$ for the 2nd virial coefficient. For the 3rd virial coefficient, $n=3$, and the variables of integration are $d\mathbf{x}d\mathbf{y}$. K , L , and U are defined by Eqs. (C.10) and (C.11). In order to obtain the expansion formulas for the higher order virial coefficients at high temperatures the Eq. (C.13) may be used, if $\mathfrak{B}$, K , L and U are appropriately defined. From the definition of Eqs. (C.10) and (C.11) it is easily seen how to define them. Eqs. (3.10) and (3.12) are easily derived from Eq. (C.13).

References

- 1) J. E. Mayer and M. G. Mayer: *Introduction to Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940) 277.
- 2) J. O. Hirschfelder, C. E. Curtiss and R. B. Bird: *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954)
- 3) T. Kihara: *Rev. Mod. Phys.* **25** (1953) 831; **27** (1955) 412.
- 4) M. L. Goldberger and E. N. Adams: *J. Chem. Phys.* **20** (1952) 240.
- 5) K. M. Watson: *Phys. Rev.* **103** (1956) 489.
- 6) J. M. Luttinger and W. Kohn: *Phys. Rev.* **109** (1958) 1892.
- 7) T. Yokota: *Ann. Inst. Stat. Math.* **10** (1959) 137.
- 8) T. Yokota: Lecture at the meeting of the Physical Society of Japan on May 31, 1957.

Theoretical Study on the Properties of Coercive Field of BaTiO_3 Single Crystal

By Ryuji ABE

Faculty of Science, Nagoya University, Nagoya, Japan

(Received September 16, 1959)

The properties of the coercive field of BaTiO_3 single crystal were investigated theoretically by using the previous result on the domain wall motion. The dependences of the coercive field on applied field, crystal thickness and temperature were discussed. Further a study on the shape of hysteresis loop was made and it was concluded that the particular shapes of the hysteresis loop such as the double hysteresis loop will be caused by the effects of internal stresses.

§ 1. Introduction

For ferromagnetic substances the "coercive field" which is given from the figure of the hysteresis loop (Fig. 1) by measuring the length $\overline{AB}$ is generally identified with the threshold field at which almost all domain walls can begin to move. For ferroelectric substances, on the contrary, the threshold field is fairly lower than the coercive field as experienced for most crystals. For the BaTiO_3 single crystal, for example, the threshold field is within a few hundreds volts/cm at room temperatures¹⁾, while the corresponding coercive field is several hundreds volts/cm or higher for 60 cps alternating field²⁾. Thus,

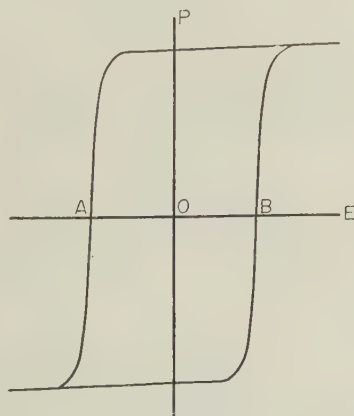


Fig. 1.

for ferroelectric substances the coercive field is not determined by the threshold field but will be determined by the characteristics of the movement of domain wall in applying the outer field.

Then how can the coercive field be represented in terms of the movement of domain

walls? And how can the hysteresis loop be related with the movement of domain walls?

The answers to these questions were given here for the simplest case i. e. for the BaTiO_3 single crystal which has only 180° domains, using the result in the previous paper³⁾. The dependences of the coercive field on applied field, crystal thickness and temperature were examined. Furthermore, the effects of imperfections on the hysteresis loop were discussed qualitatively, and it was concluded that the loop may become double if the crystal is heavily stressed. This conclusion will be useful in interpreting the various features of the damage of crystals such as rochelle salt⁴⁾ and triglycine sulfate⁵⁾ caused by γ -ray irradiation.

§ 2. Theoretical Expression Coercive Field

To obtain the theoretical expression of the

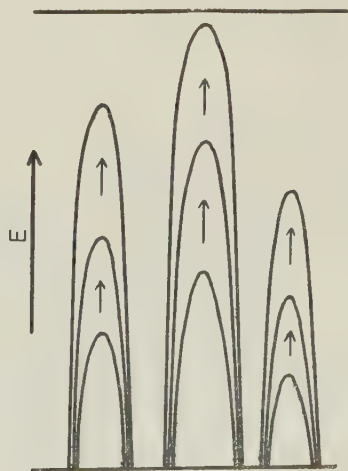


Fig. 2. The arrows indicate the growth process of the original spike-shaped domains.

"coercive field", let us assume that the growth of the 180° domain is mainly caused by the forward growth of the domain, i. e., the growth in the direction of applied field (Fig. 2). This assumption is based on the direct observation of the forward growth by Merz²⁾†. If it is assumed further that the switching time of the domain is determined mainly by the velocity of the forward growth, the "coercive field" can be determined as follows: now let us call the velocity of the forward growth of the domain v_o ††. Assuming that all domains have nearly the same magnitude and play similarly in applying the outer field, the following relations can be obtained:

$$a_o = \int_0^{t_s} v_o dt = \int_0^{E_o} v_o \frac{dt}{dE} dE, \quad (1)$$

where d_o is the thickness of the crystal, t_s is the switching time and E_o is the coercive field. E is related with t by a certain functional relation. For the sinusoidal wave $E = E_o \sin \omega t$ where E_o is the amplitude of applied field and ω is the frequency multiplied by 2π . Then using the relation

$$\frac{dE}{dt} = E_o \omega \sqrt{1 - (E/E_o)^2}, \quad (E \leq E_o) \quad (2)$$

(1) becomes

$$d_o E_o \omega = \int_0^{E_o} v_o \frac{dE}{\sqrt{1 - (E/E_o)^2}} \quad (3)$$

From this relation the coercive field can be calculated, if the dependence of v_o on E is known.

§ 3. Quantitative Examination of Coercive Field

According to the result in the previous paper³⁾, the forward growth of 180° domain in the BaTiO₃ single crystal is caused by the successive random movement of the various parts of the front wall and by the rearrangement of these local walls due to the effects of depolarizing field which rules out the shapes

† Recently by Miller and Savage⁶⁾ the sidewise growth of 180° domain has been observed. For such case the present treatment can be also applied with a slight modification of the notation i.e. by replacing v_o and d_o in Eq. (1) by v_n and d_a , where v_n is the velocity of the 180° wall normal to the surface and d_a is the breadth of the domain.

†† The meaning of the velocity v_o will be discussed later.

of the front wall that increase the depolarizing energy. Therefore the displacement of the front wall will actually be different at every part of the front wall owing to the effects of depolarizing field. Let us assume, however, as a rough approximation that every part of the front wall of a domain moves by an equal distance per unit time in the direction of applied field. Then the time taken by the front wall to move by a unit spacing can be written as

$$\Delta t = \frac{n}{p^*}, \quad (4)$$

where p^* is the probability per unit time with which the local wall having a certain front area††† can shift by a unit spacing and n is the number of the transitions that take place until the whole front wall has just shifted by a unit spacing. From the result in the previous paper³⁾, the number n is given as

$$n = \frac{S_o}{ms^*u}, \quad (5)$$

where S_o is a certain area of the front wall of a domain which will be shifted without the effects of depolarizing field††††, s^*u is the front area of the local wall and m is the number of the local walls which can move simultaneously. The velocity of the domain become then

$$v_o = \frac{u}{\Delta t} = \frac{mu^2 s^* p^*}{S_o}. \quad (6)$$

Using the relation $s^*u p^* = (d_o/2P_s) i_{\text{local}}^*$ in the previous paper³⁾, this is rewritten as

$$v_o = \frac{mvd_o}{2P_s S_o} i_{\text{local}}^*, \quad (6')$$

where i_{local}^* is the current caused by the movement of the local wall. Substituting (6') into (3) gives

$$d_o E_o \omega = \int_0^{E_o} \frac{mud_o}{2P_s S_o} i_{\text{local}}^* \frac{dE}{\sqrt{1 - (E/E_o)^2}}. \quad (7)$$

Except at very high frequencies, the observed coercive field is lower than the critical field E' which has been defined and determined in the previous paper³⁾. Then, using the relation

††† The magnitude of the front area is determined under the condition that the current induced by the movement of the local wall is maximum.

†††† If the effects of depolarizing field is neglected at all, S_o equals the whole area of the front wall of the domain.

$$i_{\text{local}}^* = \frac{4P_s \nu u^2 \sigma_w}{a_0 \sigma^*} \exp\left(-\frac{\sigma_w \sigma^* \nu}{k T E P_s}\right) \quad (E \ll E') \tag{8}$$

in the previous paper³⁾, (7) becomes

$$d_0 E_0 \omega = \int_0^{E_0} \frac{2 \nu u^3 m \sigma_w}{\sigma^* S_0 \sqrt{1 - (E/E_0)^2}} \exp\left(-\frac{\sigma_w \sigma^* u}{k T E P_s}\right) dE, \tag{9}$$

which is rewritten as

$$\frac{\sigma^* S_0 d_0 E_0 \omega}{2 m \nu u^3 \sigma_w} = \int_0^{E_0} \frac{1}{\sqrt{1 - (E/E_0)^2}} \exp\left(-\frac{\sigma_w \sigma^* u}{k T E P_s}\right) dE, \tag{9'}$$

where σ^* is the activation energy for the local wall to move by a unit lattice spacing in the direction of applied field, σ_w is the 180° wall energy, ν is the thermal frequency of Ti ion and u is the unit lattice spacing. Thus the fundamental equation to calculate the coercive field in various conditions is obtained.

Now, using the data in the previous paper³⁾, let us calculate the magnitude of the coercive field and examine the dependences of the coercive field on amplitude and frequency of applied field, crystal thickness and temperature. Using the data³⁾ that

$$\frac{S_0}{m \nu} \sim 5 \times 10^{-27} \text{ cm}^2 \text{ sec} \quad \text{and} \quad \sigma^* = 1.6 \text{ esu} \quad (\text{at } 23^\circ\text{C})$$

and putting $\sigma_w = 1.40 \text{ esu}$, $kT = 4 \times 10^{-14} \text{ esu}$ and $u = 4 \times 10 \text{ cm}$, (9') becomes

$$4 \sim 5 \times 10^{-5} E_0 \omega d_0 = \int_0^{E_0} \frac{\exp - (28.6/E)}{\sqrt{1 - (E/E_0)^2}} dE. \tag{10}$$

Assuming that $E_0 = 10^4 \text{ volts/cm}$, $\omega = 2\pi \times 60$ and $d_0 = 5 \times 10^{-3} \text{ cm}$, the coercive field is calculated to be

$$E_c = 1500 \sim 1600 \text{ volts/cm}$$

This value is a few times higher than Merz's experimental value²⁾. This difference, however, may not be so significant because the magnitude of the observed coercive field is fairly different for different crystals†.

The dependence of the coercive field on amplitude is shown in Fig. 3 and the dependences of the coercive field on frequency and crystal thickness are shown in Fig. 4. It will be seen from Fig. 4 that $\log \omega$ or $\log d_0$ changes nearly linearly with $1/E_c$ except for very high frequencies.

The dependence of the coercive field on temperature can not be determined precisely because the temperature dependences of a few quantities in (9') are not known. However the rough estimation of the dependence can be obtained from the following consideration.

Since the dependence is mainly determined

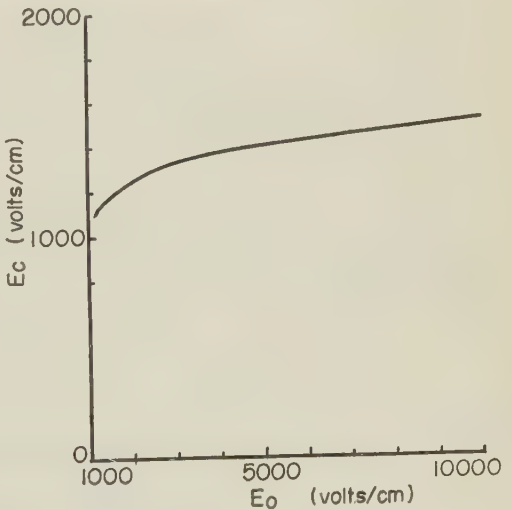


Fig. 3. Coercive field versus amplitude of applied field.

by the exponential term in (9'), neglecting the temperature dependences of the other terms, the dependence becomes

$$E_c \propto \frac{\sigma_w \sigma^* u}{k T P_s}. \tag{11}$$

According to Kinase and Takahashi³⁾, σ_w is

† The coercive field is reported by Wieder⁷⁾ to be about a few thousand volts/cm at room temperatures.

nearly proportional to P_s^2 . Then assuming that σ^* is proportional to P_s^n , (11) reduces to

$$E_c \propto \frac{P_s^{n+1}}{T^n}.$$

(12)

This result indicates that the coercive field for the BaTiO₃ crystal decreases abruptly with the decrease of the spontaneous polarization.

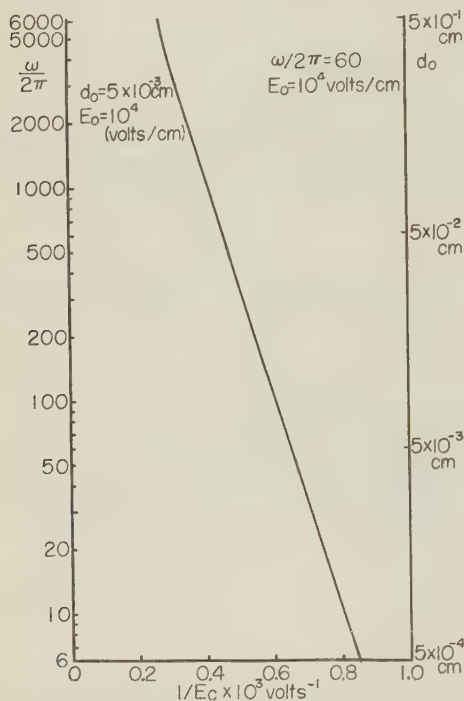


Fig. 4. Reciprocal of coercive field versus applied frequency and crystal thickness.

§ 4. Effects of Internal Stresses on Hysteresis Loop

In the present section let us consider the

effects of internal stresses on the hysteresis loop. In this connection let us consider how the stresses influence the stability of domains. Suppose at first there are no internal stresses in the crystal. Since in the experimental condition that the outer field is applied by a constant-voltage source, the polarizing charges on the surfaces which are caused by the movement of domains are always compensated by the charges on the electrodes, the effects of depolarizing field can entirely neglected. Then the state of the crystal which is fully polarized in one direction will be most stable, because by the appearance of domain walls the free energy of the crystal is increased by the energies of the boundaries. On the contrary, if a certain internal stresses exist in the crystal, the state with a certain domain configuration may become most stable, because the internal stresses will be relaxed by the appearance of domains. Therefore, for such crystals the original state with a certain domain configuration may be restored when the applied field has been removed. Thus the internal stresses will act on the domain walls as a sort of restoring force.

To introduce these effects into calculation, let us assume that, by the existence of the internal stresses, the wall energy at the position (X, Y, Z) is modified by $U(X, Y, Z)$ per cm³, where the coordinate Z is parallel to the applied field. Then, as done in the previous paper³⁾, the change of free energy of the local wall in the intermediate state ΔF^M and in the final state ΔF^F can be written respectively as

$$\Delta F^M = -EP_s\Delta V + \frac{\sigma^*}{u}\Delta V$$

(13)

and

$$\begin{aligned} \Delta F^F &= -2EP_s\Delta V + \sigma_w\Delta S + (U(X, Y, Z+u) - U(X, Y, Z))\Delta V \\ &= -2EP_s\Delta V + \sigma_w\Delta S + \frac{\partial U}{\partial Z} \cdot u \cdot \Delta V \end{aligned}$$

(14)

where ΔV and ΔS are the increase of volume and surface of the initial domain respectively. The increase of U in the intermediate state is neglected here, because it will be generally much smaller than σ^*/u . The transition probability of the local wall by unit lattice spacing in the direction of applied field becomes then

$$p^* = \frac{2\nu u^2}{kT} \left(s^* \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right) - \sigma_w \right) \exp - \frac{\sigma^* s^* u}{kT}$$

(16)

where

$$s^* = \frac{2A + BC + \sqrt{4A^2 + B^2 C^2}}{2AC}$$

and

$$A = \frac{2P_s \nu u^4}{d_0 k T} \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right),$$

$$B = \frac{4P_s \nu u^4 \sigma_w}{d_0 k T} \quad \text{and} \quad C = \frac{\sigma^* u}{k T}.$$

This relation can be simplified when $2A \ll BC$, i.e. $E \ll E'$, to

$$p^* = \frac{2\nu u}{\sigma^*} \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right) \exp \left(- \frac{\sigma_w \sigma^* u}{k T \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right)} \right) \quad (17)$$

and then the maximum local current become, as in the previous paper,

$$i_{\text{local}}^* = \frac{4P_s \nu u^3 \sigma_w}{d_0 \sigma^*} \exp \left(- \frac{\sigma_w \sigma^* u}{k T \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right)} \right), \quad (18)$$

from which the hysteresis loop can be obtained by the process similar to the previous one. For the present case, however, the treatment is in general rather complicated because the local current is generally different at every position of the front wall and so the simple relations (4) and (5) can not be applied. Since, further, the generalization of the previous treatment will not be useful in discussing the qualitative features of the hysteresis loop, the discussion will be confined to the case that the gradient $\partial U / \partial Z$ is a function of Z only, which can be treated without the generalization. With the help of (6'), the velocity of the domain is then written as

$$v_o = \frac{2\nu u^4 \sigma_w m}{S_0 \sigma^*} \exp \left(- \frac{\sigma_w \sigma^* u}{k T \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right)} \right). \quad (19)$$

Since the change of the crystal polarization within a short time can be written as

$$\frac{dP}{P_s} = \frac{v_o dt}{d_0} = \frac{v_o}{d_0} dE \cdot \frac{dt}{dE} \quad (20)$$

if all domains move similarly with the velocity $v_o^{\dagger\dagger}$, the change of polarization with the change of applied field is given, using (2) and (20), by

$$\frac{dP}{dE} = \frac{2\nu u^4 \sigma_w m P_s}{S_0 \sigma^* d_0 E_0 \omega \sqrt{1 - (E/E_0)^2}} \exp \left(- \frac{\sigma_w \sigma^* u}{k T \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right)} \right). \quad (21)$$

† When $2A \gg BC$ i.e. $E \gg E'$, the transition probability becomes

$$p^* = \frac{2\nu u}{k T} \left(\frac{2k T}{\sigma^*} \left(EP_s - \frac{1}{2} \frac{\partial U}{\partial Z} \cdot u \right) - \sigma_w u \right) e^{-2}.$$

As stated in the previous section, this relation is useful only when the frequency of applied field is very high.

†† A better modification can be obtained by assuming that the velocity v_o may be different for each domain. (20) is then modified to

$$\frac{dP}{P_s} = \sum_i v_o^i \frac{S_i}{S} \frac{dt}{d_0}$$

where v_o^i and S_i are the velocity and front area of i -th domain respectively and S is the area of the electrode. Then the hysteresis loop can be determined from the relation

$$\frac{dP}{dE} = \frac{P_s}{d_0 E_0 \omega \sqrt{1 - (E/E_0)^2}} \sum v_o^i S_i.$$

From this relation the whole shape of the hysteresis loop can be determined if the dependence of U on Z is known.

Some of the calculated hysteresis loops are shown schematically in Fig. 5 and Fig. 6. The relation between the energy U versus Z for each hysteresis loop is shown on the left side of each loop. It will be seen from these figures that the sharper the gradient, $\partial U/\partial Z$,

recognized that the rochelle salt crystal nearly recovers the original domain pattern when the applield is removed. This fact is also ascertained by the optical measurement⁹⁾ which can detect the resultant movement of all domains. According to the above conclusion the recovery is not caused by the polarizing charges, but by the internal stresses in the crystal. These internal stresses will act on the crystal as a sort of restoring force

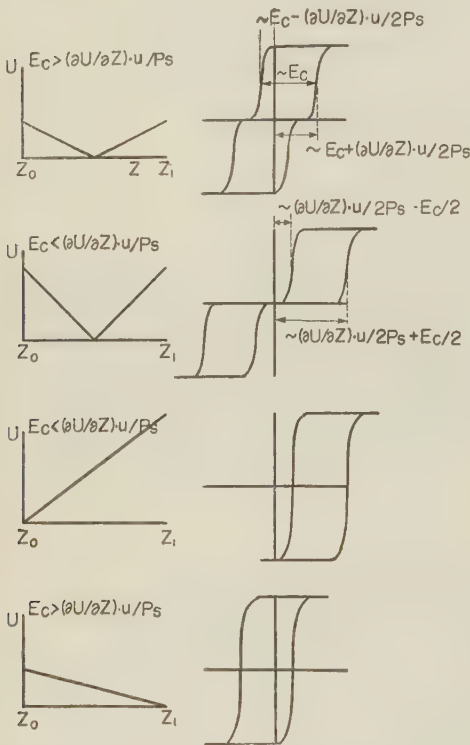


Fig. 5. Deformation of hysteresis loops by internal stresses.

becomes, the more the hysteresis loop is deformed. This fact is also immediately seen from (21). That is, if $\partial U/\partial Z$ is positive and the applied field E is lower than $(\partial U/\partial Z)u/2P_s$, $(EP_s - (1/2)(\partial U/\partial Z)u)$ becomes negative. Then the domain walls can not move in the direction of applied field and they will be clamped at a certain stable position until the applied field reaches the critical field $(\partial U/\partial Z)u/2P_s$. Thus it will be easily understood that the hysteresis loop becomes double when the crystal is heavily stressed.

§ 5. Discussion

1) Through the direct observation of domains by polarizing microscope, it has been

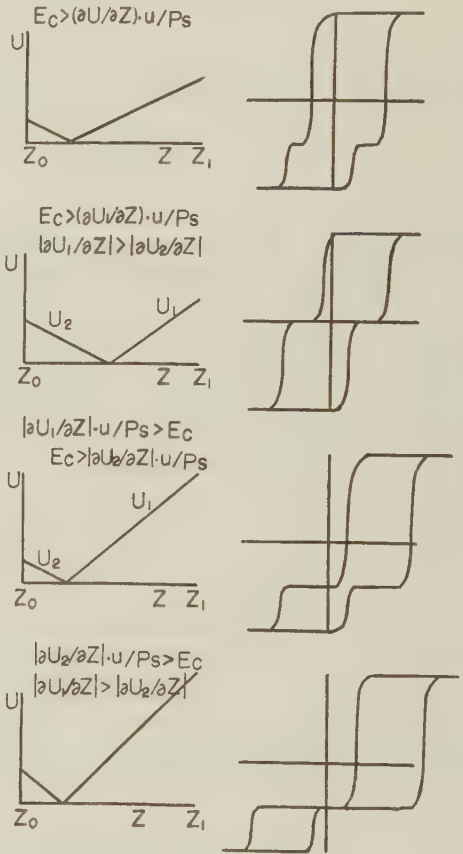


Fig. 6. Deformation of hysteresis loops by internal stresses. Z_0 and Z_1 indicate the coordinates of the crystal surface normal to c-axis.

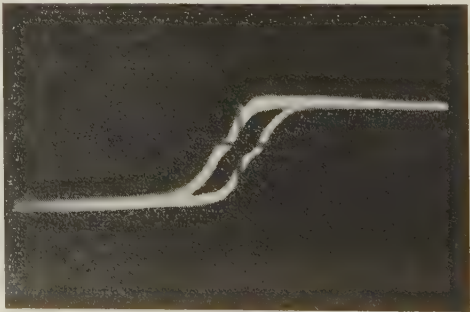


Fig. 7.

to deform the shape of the hysteresis loop, as discussed in the previous section. In fact, the deformation of the hysteresis loop is frequently seen, especially when the crystal has been left for a long time without applying any field, indicating that, by the gradual reorientation of imperfections, a certain domain configuration becomes more stable. One example is shown in Fig. 7.

2) Recently it has been reported by Chynoweth⁵⁾ that the hysteresis loop of triglycine sulfate is heavily deformed by γ -ray irradiation, as observed for rochelle salt⁴⁾. According to his result, the hysteresis loop is little deformed, even if the crystal is irradiated heavily by γ -ray, so long as an alternating field is being applied. However, once the field is removed and it is applied again a few minutes later, the hysteresis loop becomes heavily deformed. This phenomenon seems to be somewhat strange but can be explained satisfactorily by considering the effects of internal stresses as follows: imperfections such as interstitial atoms and vacancies will be created by the γ -ray in every part of the crystal. They will be in activated and non-equilibrium states and so tend to move through the crystal lattice and gather at the domain boundaries or the portions with internal stress, decreasing the total free energy. However, if the crystal has no internal strains and the alternating field is being applied, such a clustering can not occur because the imperfections

can not follow the fairly rapid movement of domain walls, and no deformation of the hysteresis loop will be expected. Once the field has been removed, the domain walls cease to move and the imperfections will gather to the walls. The clusters of the imperfections thus formed will act on the walls as a sort of restoring force. Thus, when the field is applied again, the deformation of the hysteresis loop will be observed. Through this explanation it will be suggested that the mobility and lifetime of the imperfections may be determined by observing the change of hysteresis loops under the different condition of irradiation under applied field.

Finally the author wishes to express his appreciation to Dr. T. Nakamura for his helpful discussions.

References

- 1) H. H. Wieder: J. Appl. Phys. **27** (1956) 413.
- 2) W. J. Merz: Phys. Rev. **95** (1954) 690.
- 3) R. Abe: J. Phys. Soc. Japan **14** (1959) 633.
- 4) I. S. Zheludev and V. A. Iurin: Bull. Acad. Sci. U. S. S. R. English translation **20** (1956) 193.
- 5) A. G. Chynoweth: Phys. Rev. **113** (1959) 159.
- 6) R. C. Miller and A. Savage: Phys. Rev. **112** (1958) 755.
- 7) H. H. Wieder: Phys. Rev. **99** (1955) 1161.
- 8) W. Kinase and H. Takahashi: J. Phys. Soc. Japan **12** (1957) 464.
- 9) R. Abe: J. Phys. Soc. Japan **13** (1958) 244.

Heitler-London Approach To Electrical Conductivity and Application to *d*-Electron Conductions

By Jiro YAMASHITA and Tatumi KUROSAWA

The Institute for Solid State Physics, University of Tokyo, Tokyo

(Received December 3, 1954)

Conduction by the movement of an extra electron which is tightly bound to an ion in an ionic lattice is discussed. We assume that the wave function of the electron is localized closely around an ion and the motion of the electron is so slow that lattice polarization is induced around the electron. Further, we assume that the potential in the lattice deviates slightly from a perfectly periodic arrangement owing to the existence of many impurity-ions. In these circumstances the current is connected with a hopping motion of the electron from ion to ion rather than with a translational motion of the electron in a nearly perfect lattice. In §2 we discuss the self-trapped state of a positive hole in a polar lattice with a fluctuating potential. In §3 we develop a theory of the transition of the hole from ion to ion by using the non-adiabatic approximation, and further in §4 we discuss the same problem by the adiabatic approximation. In the last section we compare the theory with experiments. The electrical conduction through *d*-electrons in the crystals such as $\text{Li}_x\text{Ni}_{1-x}\text{O}$, $\text{LaMnO}_3+\text{SrMnO}_3$, magnetite and CoFe_2O_4 is regarded as good examples to which the Heitler-London conduction mechanism is applicable. We also discuss the impurity conduction in germanium from a similar point of view.

§ 1. Introduction

In the previous paper¹⁾, which will be referred to as I, we discussed some characteristics of the current observed in NiO and LaMnO_3 crystals. In these crystals the mobility of electrons is quite small as compared with that in usual semiconductors. Moreover, the temperature dependence of the mobility is also complicated according to a total amount of impurity-ions which controls the conductivity. In some specimens the mobility is nearly constant, and in others it increases with increasing temperature. In these cases the conduction mechanism may not be explained by the usual band theory. A formal application of the band theory to these cases leads to rather unreasonable results, for example, the mean free path of electrons being much smaller than the lattice constant. Therefore, we thought it worth while to approach the problem from the opposite direction. We have developed a theory of the electrical conductivity on the basis of the Heitler-London approach and applied it to interpret the observed current in NiO and LaMnO_3 . Although the theory is

oversimplified in some respects, it gives a qualitative explanation of the main features of the current. In the previous treatment, however, we introduced a model rather intuitively, and we did not investigate the foundation of the theory. The purpose of the present paper is to discuss the foundation of the H-L approach to the conductivity and make clear the condition under which this approach is applicable. Another purpose of the present paper is to illustrate some examples to which the present model seems to be applicable.

The problem why the nickel oxide crystal is an insulator is one of the fundamental, but difficult problems in solid state physics. A qualitative explanation has been given by Mott²⁾. Let us imagine an assembly of N positive ions making a regular lattice and N electrons. When the lattice spacing is sufficiently small, the ground state of this system is well represented by a simple energy band picture. The N electrons fill a lower half of the state in the energy band and this system will be a good conductor. Since the correlation effect between electrons with anti-

parallel spin is not considered in the simple band picture, the system contains too many numbers of negative ions. This situation is unfavorable for the cohesive energy of the system. However, by forming a band the system can reduce its kinetic energy, so that this gain is able to compensate a large part of the energy loss mentioned before when the band width is sufficiently wide. On the other hand, when the lattice spacing is large, the energy loss caused by the negative ions cannot be balanced by the energy gain due to the formation of an energy band. Therefore, it is supposed that the H-L picture is more favorable when the lattice spacing is large. If we compute the energy of the system by the both approximations as a function of the lattice spacing, we may have a rough idea about the applicable range of each approximation. We must, however, notice that the both approximations may be useful only in their ideal or nearly ideal cases, but too crude to discuss the nature of the crystal in the intermediate region. At any rate, we may say that the simple band picture has a limit of its applicability, and the NiO crystal seems to be outside of the limit. Since the Bloch approach to the electrical conductivity is intimately connected with the band picture, the failure of the band approach in the cohesive energy suggests inadequacy of the Bloch picture of the conductivity.

The pure NiO crystal is a good insulator, but it becomes a semiconductor when some of the Ni^{++} ions are replaced by Li^+ ions. This replacement introduces the Ni^{3+} ions in the lattice to preserve the electrical neutrality of the crystal as a whole. We may interpret this Ni^{3+} ion as a positive hole captured at a Ni^{++} ion. The holes of Ni^{++} ions are not, however, bound to definite positions in the lattice, but may wander through the crystal by jumping from ion to ion. This possibility of random wandering gives rise to electrical conduction. A theory of this type, the H-L approach, seems to be suitable to interpret the very small mobility observed in NiO and other crystals. A serious objection might arise to this approach. Why does a hole in NiO behave like a slowly moving self-trapped hole, but not like a usual polaron? Since the crystal has a perio-

dic structure, the effective potential to the hole is also periodic and consequently the ground state of a hole should be represented by a running wave solution of the Schrödinger equation.

In Appendix I, however, we show that we can imagine a self-trapped state for a hole when the wave function of the hole is well localized around an ion and the polarization of a lattice is sufficiently large, because the energy of the self-trapped state is lower than the usual polaron state. However, one may argue that one can still construct a crystal wave function of the Bloch type by superposing the wave function of the hole self-trapped at a certain lattice point, if the crystal has a perfect periodicity. In a real crystal, especially in a NiOLi_2O alloy which we consider, this periodic condition is by no means realized. If the state of the system is represented by an energy band of a considerable width, a small fluctuation from the periodic potential is regarded as a small perturbation, but for a translational motion of a heavy hole accompanied by a large polarization a small deviation from the periodic potential has a decisive influence and we can no more describe the motion of the hole as a propagation of wave in a periodic lattice.*

In general, we may classify conduction mechanism into three cases according to the strength of electron-lattice interaction. (a) When the effective mass of electrons is small and the electron-lattice interaction is sufficiently weak, the state of the electron is described by a set of the wave number vectors k . Then, the electron-lattice interaction causes transitions between these states with

* Even when we disregard the fluctuation of the periodic potential, it is not necessarily true that the motion of the hole should be described by a wave motion. The translational motion of the hole is possible through two alternative ways, one through the propagating motion of a wave and the other through the transition from one ion to another with emission and absorption of phonons. If the wave function is localized tightly around an ion and the polarization induced around the hole is large, the latter process becomes predominant because of a very heavy effective mass of the hole. In the paper I, we treated such an ideal case without considering the fluctuation of the periodic potential. We think, however, that the assumption of the present paper is more plausible.

k and k' respectively. This transition is regarded as a Markoff process, so that the statistical behaviour of the electrons is well represented by the Bloch equation. (b) When the effective mass of the electrons is considerably large or the electron-lattice interaction is strong as in the case of conduction electrons in alkali halide crystals at room temperature, we can no longer treat the interaction as a small perturbation. Then, we do not know what state can be regarded as a well defined stationary state, and consequently we cannot find a suitable Markoff process. (c) However, if the effective mass of the electrons becomes large enough and the interaction with the lattice is also very strong, the approach from the opposite direction may have a meaning, and then the problem is again manageable. In this case, the state which is localized around an ion may be regarded approximately as a stationary state and the effect of other ions is regarded as a perturbation. The electron makes a transition from ion to ion by the perturbation with a certain probability. This transition of the electron is accompanied with emission and absorption of many phonons. In the forth-coming paper one of the authors of the present paper (K) will discuss the nature of this transition in detail. The result is that this transition is a Markoff process and statistical behaviour of the electrons is represented by the diffusion equation. Following the method developed by Van Hove³⁾ we prove that such a wandering motion of the electron obeys a law

$$\frac{dP_n(t)}{dt} = \sum_{n'} (W(n, n')P_{n'}(t) - W(n', n)P_n(t)),$$

where $P_n(t)$ is the probability that an electron is situated at the ion n at the time t , and $W(n, n')$ is the probability of the transition of the electron from the ion n' to the ion n .

Next, we discuss briefly the condition under which the H-L approach is permissible. The first condition is that the localized state is possible on the energy consideration. The second condition is that the life time of the localized state should be sufficiently long as compared with a period of the lattice vibration, because it takes a time of the order of the lattice vibration to induce lattice polarization around the hole. Therefore, the condition is:

$$\nu \gg W.$$

According to the Einstein relation we can determine the mobility from the transition probability W :

$$\mu = (ea^2/kT)W,$$

where a is the distance between nearest neighbour ions. Inserting the values $T=300^\circ\text{K}$, $a=4\times 10^{-8}\text{cm}$ and $W=10^{13}\text{sec}^{-1}$ we have:

$$\mu \sim 0.6\text{cm}^2/\text{volt sec}.$$

Next, let us investigate a condition for the Bloch theory of the conductivity. We set a condition for it:

$$h/\text{band with} \ll \tau.$$

If we estimate the band width by $\hbar^2 k_0^2/2m$, where k_0 is nearly equal to π/a we have:

$$\mu = \frac{e}{m}\tau \gg \frac{4}{\pi} \frac{ea^2}{\hbar} \sim 2\text{cm}^2/\text{volt sec}.$$

This condition gives the lower bound of the mobility for the usual Bloch theory. Thus, we may roughly determine the border-line of the two alternative approach. When the mobility is much larger than one $\text{cm}^2/\text{volt sec}$, the usual Bloch theory is applicable, while the H-L approach may be better when the mobility is much smaller than one $\text{cm}^2/\text{volt sec}$. If the mobility is near the border-line as in the case of a polaron in some ionic crystals above room temperature ($10 > \mu > 0.1$), neither approaches seem to be accurate enough.

As mentioned in the paper I we expect that the temperature dependence of the mobility shows special characteristics in the H-L picture. In the usual Bloch picture the mobility should decrease with increasing temperature. In some compounds, however, the mobility is observed to increase with increasing temperature. This fact is another important character which suggests a necessity of the H-L approach which is developed in the present paper. Hitherto we have mentioned the current in polar crystals from the standpoint of the H-L picture. However, this picture is also applicable to non-polar crystals, if some conditions are fulfilled in them. We shall show that the impurity conduction in germanium is a typical example of this picture when the concentration of impurity atoms is very small.

Finally we mention about applications of theory to real crystals. We believe that the theory is applicable to the conduction phenomena observed in some compound which have a transition element as a constituent, although many of experimental facts are not necessarily conclusive at the present stage of development. We may count NiO, MnO, Fe₂O₃, V₂O₃, Ti₂O₃ and LaMnO₃ as examples of such materials, and the magnetite may be another example. However, it is a rather difficult task to draw a quantitative conclusion from a simplified theory. Even in the Bloch theory we have a few examples which can be treated quantitatively, because we have no reliable knowledge about the band structure, the interaction constant and so on. The situation is much worse both experimentally and theoretically in the compounds which we want to study, so that the discussion remains inevitably ambiguous, but we want to stress that the problem is a matter of the principle whether the usual band theory is valid or the H-L approach is better for the cases mentioned previously. For that purpose the qualitative discussions are sometimes quite useful, and we hope that the present paper will give some contributions to this problem.

§2. A Tightly Bound Electron in a Polar Lattice

In the H-L approach to the conductivity the most important quantity is the transition probability from one localized state to an adjacent localized state with nearly the same energy, because the spatial motion of electron is fully described by this quantity. In order to evaluate the transition probability it is convenient to consider two cases separately: (1) the transition takes place in a manner that the adiabatic approximation is allowable, and (2) it is not allowable. We shall discuss the non-adiabatic case in sections 2 and 3, and the adiabatic case in section 4.

Let us imagine an electron (or a positive hole) in a lattice. We denote the lattice sites as $\vec{R}_n$. The Hamiltonian of the system is written as

$$H = \frac{p^2}{2m} + eU_t(\vec{r}) + V(\vec{X}_1, \dots, \vec{X}_N) + \sum_{n=1}^N K_n, \quad (1)$$

where $p^2/2m$ is the kinetic energy of the electron, m is the electron mass, $\vec{r}$ is the position vector of the electron, $\vec{X}_n$ is a position vector of the n -th ion which is not necessarily equal to $\vec{R}_n$, $U_t(\vec{r})$ is the total potential of the lattice for the electron:

$$U_t(\vec{r}) = \sum_{n=1}^N U(\vec{r} - \vec{X}_n) + \Delta U(\vec{r}). \quad (2)$$

Here $U(\vec{r} - \vec{X}_n)$ is a potential due to the ion n . If the lattice were perfect, the total potential of the lattice would be given by the sum $\sum U(\vec{r} - \vec{X}_n)$. In fact, the potential exerting on the electron is not perfectly periodic, but fluctuates slightly ion by ion, because the lattice contains a fair number of impurity ions and excess electrons. This situation is taken into account by the term $\Delta U(\vec{r})$ in (2). Further, $V(\vec{X}_1, \dots, \vec{X}_N)$ is the interaction energy between the N ions and K_n is the kinetic energy of the n -th ion. Then, the motion of the system is represented by

$$H\Psi(\vec{r}; \vec{X}_1, \dots, \vec{X}_N) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}; \vec{X}_1, \dots, \vec{X}_N). \quad (3)$$

In general, it is very difficult to solve the equation (3), but we are able to find an approximate property of the solution of (3) under some special assumptions.

Let us imagine that an electron is tightly bound to a certain ion which will be referred to as the ion 1. If the life time of that state is long enough as compared with the period of the lattice vibration, then the electric polarization—more generally lattice distortion—is induced around the electron and contributes to stabilize that configuration. In order to describe this situation we consider the following part of the previous Hamiltonian:

$$\begin{aligned} H^{(1)} = & \frac{p^2}{2m} + eU(\vec{r} - \vec{X}_1) \\ & + e \sum_{n \neq 1}^N [U(\vec{r} - \vec{X}_n) - U(\vec{r} - \vec{R}_n)] \\ & + V(\vec{X}_1, \dots, \vec{X}_N) + e\Delta U(\vec{r}). \end{aligned} \quad (4)$$

If $\vec{X}_n - \vec{R}_n$ is not large, the third term makes a nearly constant potential in the vicinity of the position $\vec{X}_1$, because it is a static potential due to the electric poles at the ions

other than the ion 1. Moreover, $\Delta U(\vec{r})$ is also regarded as a slowly varying potential as compared with the potential $U(\vec{r}-\vec{X}_1)$. Under the assumption that the potential $U(\vec{r}-\vec{X}_1)$ is fairly large and the wave function of the electron is well localized around $\vec{X}_1$, we may expect that these additional potentials cause only a small change to the original wave function of the ion 1, and the wave function of the electron depends slightly upon $\vec{X}_n$. Since the eigenvalues of $H^{(1)}$ is a function of $\vec{X}_n$, we introduce a set of the coordinates of the ions ($\mathbf{X}_0^{(1)}$), ($\equiv \vec{X}_{10}^{(1)}, \dots, \vec{X}_{n0}^{(1)}, \dots$), which represents the energy-minimum configuration of the lattice when the electron is localized around the ion 1. Thus the wave function of the Hamiltonian ($H^{(1)} + \sum K_n$) is approximately given by a product of the electronic wave function $\phi(\vec{r}-\vec{R}_1)$ and the lattice wave function corresponding to the oscillating motion around the minimum configuration ($\mathbf{X}_0^{(1)}$). If we expand the eigenvalue of $H^{(1)}$ with respect to $(\vec{X}_n - \vec{X}_{n0}^{(1)})$ up to quadratic terms, the motion of the lattice is represented by a set of simple harmonic oscillations. Since the variables $(\vec{X}_n - \vec{X}_{n0}^{(1)})$ are not the normal coordinates of the motion, we must introduce a set of the normal coordinates. Here we do not investigate them in detail, but only denote them as $Q_n^{(1)}$. Then the wave function of the system is given by*

$$\Psi_m = \phi(\vec{r}-\vec{R}_m) \prod_n \Phi_{n, N_n}(Q_n^{(m)}), \quad (5)$$

when the electron is localized around the ion m . Here $\phi(\vec{r}-\vec{R}_m)$ is the ground state eigenfunction of the Hamiltonian†

$$\begin{aligned} H_{ele}^{(m)} = & \frac{p^2}{2m} + eU(\vec{r}-\vec{R}_m) \\ & + e \sum_{n \neq m} [U(\vec{r}-\vec{X}_{n0}^{(m)}) - U(\vec{r}-\vec{R}_n)] + e\Delta U \end{aligned} \quad (6)$$

* Here we restrict the discussion to polar crystals, but the extension of the present formalism to non-polar crystals is quite easy.

† In the paper I we discussed the problem by the continuum model. It is a rather trivial task to demonstrate a relation between the two approximation.

and $\Phi_{n, N_n}(Q_n^{(m)})$ is the wave function of the n -th harmonic oscillator in the state N_n . Since the electron is able to situate at any one of the ions in the lattice, the electron can jump from one lattice point to the other with a certain probability by the aid of the perturbation $\Delta H = \sum_{n \neq m} U(\vec{r}-\vec{R}_n)$. In this case

the electron must emit or absorb a number of phonons, because the potential energy ($\phi_m | \Delta U | \phi_m$) is not exactly the same before and after the transition. In the next section we shall discuss the transition probability.

§ 3. Transition Probability (non-adiabatic case)

The transition probability for transfer of the hole from the $\vec{R}_m$ ion to the $\vec{R}_{m+1}$ ion by the perturbation ΔH has been evaluated in the paper I, but with the special assumptions. In that treatment we disregarded the fluctuation of the crystal potential from the perfect periodicity. Then, there exists some extent of coherency between the wave function of the hole at different lattice points, so that the hole can make a translational motion as a propagating wave, although the velocity of the motion of this kind is quite small as compared with that of the hopping motion of the hole accompanied with emission and absorption of many phonons when the hole is tightly bound to the ion by a deep potential and a large polarization. In the present paper we take the fluctuation of the potential into account. The magnitude of the fluctuation is assumed to be larger than the width of the energy level of the hole. Then the transition of the hole must be accompanied with emission and absorption of many phonons and there is no possibility of the motion as a propagating wave. Since there are many degrees of freedom in the phonon system, the motion of the hole through such process may be regarded as a Markoff process.

The transition probability which we want to obtain is written as

$$\begin{aligned} W(\Delta E) = & \frac{2\pi}{\hbar} \frac{|M|^2}{\partial E} \\ & \times \sum_{N_n'} \sum_{N_n''} \prod_n p_{N_n'} | \langle \Phi_{n, N_n'}(m) | \Phi_{n, N_n''}(m+1) \rangle |^2. \end{aligned} \quad (7)$$

Here, M is the transition matrix element of ΔH^* :

$$M = \int \phi^*(\vec{r} - \vec{R}_m) \Delta H \phi(\vec{r} - \vec{R}_{m+1}) d\tau \quad (8)$$

and $p_{N_n'}$ is the weight of the oscillator n in a state N_n' ,

$$p_{N_n'} = \exp(-N_n' \hbar \omega_n / kT) / \sum_{N_n} \exp(-N_n \hbar \omega_n / kT), \quad (9)$$

where N_n' is a quantum number of the harmonic oscillator n . The summation is taken over all values of N_n' and N_n'' which satisfy the condition

$$-\frac{\partial E}{2} \leq \sum_n (N_n'' - N_n') \hbar \omega_n + \Delta E \leq \frac{\partial E}{2}, \quad (10)$$

where ΔE means the difference of the potential energy between the atomic cells before and after the transition:

$$\Delta E = \Delta U(\vec{R}_{m+1}) - \Delta U(\vec{R}_m). \quad (11)$$

Since the direction of the $3N$ -dimensional vector $(\mathbf{X}_0^{(m+1)} - \mathbf{X}_0^{(m)})$ does not generally coincide with the direction of any normal mode of the harmonic oscillation about $(\mathbf{X}_0^{(m)})$, the complex change of phonon states takes place at the transition. In general, it is quite difficult to compute the transition probability from (7), because we have no knowledge about the frequency spectrum of phonons and the vector $(\mathbf{X}_0^{(m+1)} - \mathbf{X}_0^{(m)})$. However, in some cases, we are able to derive more simple approximate formulas of the transition probability from (7). First, we assume that $\omega_n = \omega_0 = \text{constant}$, and then Eq. (7) is easily reduced to the following simple expression:⁴⁾

$$W(\Delta E) = \frac{2\pi}{\hbar} |M|^2 F(\Delta E) \quad (12)$$

and

$$F(\Delta E) = \sum_{p=-\infty}^{\infty} \exp\{-S(2N_0+1)\} I_p(2S\sqrt{N_0(N_0+1)}) \exp\left(-\frac{p\hbar\omega_0}{2kT}\right) \delta(\Delta E - p\hbar\omega_0), \quad (13)$$

where

$$I_p(z) = \frac{1}{2\pi} \int_0^{2\pi} \exp\{ipx + z \cos x\} dx, \quad (p = \text{integer}) \quad (14)$$

$$N_0 = 1/[\exp(\hbar\omega_0/kT) - 1] \quad (15)$$

and the quantity S is a parameter which gives the intensity of the electron-lattice interaction and defined as

$$S = \frac{1}{\hbar\omega_0} \{E^{(m)}(\mathbf{X}_0^{(m+1)}) - E^{(m)}(\mathbf{X}_0^{(m)})\}. \quad (16)$$

Here $E^{(m)}(\mathbf{X}_0^{(m)})$ is the eigenvalue of the Hamiltonian $H^{(m)}$ when the lattice takes the configuration $(\mathbf{X}_0^{(m)})$ and $E^{(m)}(\mathbf{X}_0^{(m+1)})$ is the similar quantity with the lattice configuration $(\mathbf{X}_0^{(m+1)})$. By using the continuum model we gave a more explicit expression of S in the paper I.

When we take into account the frequency dispersion of the optical variation, the problem is difficult to solve accurately. However, if the dispersion of the frequency is small, we

* Here we understand that the integral sign contains the summation over the spin coordinates. So long as we disregard the spin-orbit coupling, the perturbation ΔH does not contain the spin operator, so that the transition will take place only between the same spin states.

are able to derive an approximate formula in the following way. Let us denote the frequency by: $\omega_n = \omega_0 + \Delta\omega_n$, then we expect that $\Delta\omega_n/\omega_0$ is small. The formula which we are to evaluate is:⁴⁾

$$W = \frac{2\pi}{\hbar} |M|^2 \int_{-\infty}^{\infty} dt \exp(i\Delta E t) / 2\pi\hbar \\ \times \exp \left\{ - \sum_{j=1} \frac{1}{2} \frac{\omega_j}{\hbar} (Q_{j0}^{(m)} - Q_{j0}^{(m+1)}) \left[\coth \left(\frac{1}{2} \beta_j \right) - i \sin(\omega_j t) \right. \right. \\ \left. \left. - \coth \left(\frac{1}{2} \beta_j \right) \cos(\omega_j t) \right] \right\},$$

where $\beta_j = \hbar\omega_j/kT$. Here we introduce an approximation that we replace a quantity $A(\omega_j)$ by $A(\omega_0)$ whenever possible. Following O'Rourke⁴⁾ we introduce a set of new variables:

$$x = \omega_0 t - \phi_0, \quad \sin \phi_j = i \sinh(\beta_j/2) \quad \text{and} \quad \cos \phi_j = \cosh(\beta_j/2).$$

Then, we have:

$$F(\Delta E) = \sum_{p=-\infty}^{\infty} \exp \{ -S(2N_0+1) \} I_p(2S\sqrt{N_0(N_0+1)}) \exp \left(-\frac{p\hbar\omega_0}{2kT} \right) f_p(\Delta E - p\hbar\omega_0), \quad (17)$$

where

$$f_p(\Delta E - p\hbar\omega_0) = [I_p(2S\sqrt{N_0(N_0+1)})]^{-1} \frac{1}{2\pi} \int_{2\pi p}^{2\pi(p+1)} \exp \left[i \left(\frac{\Delta E}{\hbar\omega_0} \right) x + S \operatorname{csch} \left(\frac{\beta_0}{2} \right) \right. \\ \times \left\{ \cos x \cdot \frac{1}{3N} \sum_j \cos \left(\frac{\Delta\omega_j}{\omega_0} x + \frac{\Delta\omega_j}{\omega_0} \phi_0 + \phi_0 - \phi_j \right) \right. \\ \left. \left. + \sin x \cdot \frac{1}{3N} \sum_j \sin \left(\frac{\Delta\omega_j}{\omega_0} x + \frac{\Delta\omega_j}{\omega_0} \phi_0 + \phi_0 - \phi_j \right) \right\} \right] dx.$$

When $\Delta\omega_j$ tends to zero, the function $f_p(\Delta E - p\hbar\omega_0)$ tends to the δ -function $\delta(\Delta E - p\hbar\omega_0)$. When $\Delta\omega_j$ are finite, the functions $f_p(\Delta E - p\hbar\omega_0)$ are finite in a certain energy interval, because ϕ_0 and ϕ_j are pure imaginary quantities. However, we do not need to have a detailed knowledge about the functions f_p . For the present purpose it is sufficient to assume that f_p is finite only in a narrow region around the energy $p\hbar\omega_0$ and satisfies the condition:

$$\int_{-\infty}^{\infty} f_p(\Delta E - p\hbar\omega_0) d(\Delta E) \simeq 1.$$

By using a series expansion of the function $I_0(z)$:

$$I_0(2S\sqrt{N_0(N_0+1)}) = \sum_{x=0}^{\infty} \{ N_0(N_0+1) S^2 \}^x / (x!)^2,$$

we see that the maximum term appears at the x_0 -th term: $x_0 \simeq S\sqrt{N_0(N_0+1)}$. The physical process which corresponds to each term in the series is that the hole jumps to the final state with absorption of x phonons and emission of the same number of phonons. Thus, the final state can approximately cover the energy interval of $\hbar\Delta\omega(8S\sqrt{N_0(N_0+1)})^{1/2}$. On the other hand, the function $I_p(z)$ corresponds to the electron-transfer process in which the total number of phonons changes by p . If the processes are well classified according to the number p , the formula of the transition probability may consist of a series of terms which are classified by p . Then, the formula like (17) with suitable function f_p may be regarded as a useful approximate formula. For our present purpose the necessary quantity is not the function $W(\Delta E)$, but the average value of $W(\Delta E)$ with respect to the probability of the final state $\rho(\Delta E)$:

$$\bar{W} = \int_{-\infty}^{\infty} \rho(\Delta E) W(\Delta E) d(\Delta E). \quad (18)$$

The function $\rho(\Delta E)$ must satisfy the condition

$$\int \rho(\Delta E) d\Delta E = 1 - \frac{n}{N}, \quad (19)$$

where n is the number of the holes which participate the conduction. Unfortunately, we have no reliable knowledge about $\rho(\Delta E)$, so we must adopt case by case somewhat arbitrary assumptions. If we assume that the variation of $\rho(\Delta E)$ as a function of ΔE is rather slow, then we may disregard the variation of $\rho(\Delta E)$ over the width of f_p . Under this assumption $\bar{W}$ is reduced to:

$$\begin{aligned} \bar{W} = & \frac{2\pi}{\hbar} |M|^2 \exp \{-S(2N_0+1)\} \sum_p \exp(-p\hbar\omega_0/2kT) \\ & \times I_p(2S\sqrt{N_0(N_0+1)}) \rho(p\hbar\omega_0). \end{aligned} \quad (20)$$

This equation may be useful, when $\rho(\Delta E)$ is slow varying and average value of the fluctuation of the potential is large.

Further, if the condition $kT > \hbar\omega_0$ and $2S\sqrt{N_0(N_0+1)} \gg 1$ are satisfied, the following approximations are permissible:

$$\rho(\Delta E) \simeq \rho(\Delta E \pm \hbar\omega_0)$$

and

$$I_p(z) \simeq \frac{e^z}{\sqrt{2\pi z}} \left\{ 1 - \frac{4p^2-1}{8z} + \dots \right\} \quad (z \gg 1),$$

which shows that $I_p(z)$ depends weakly upon p . By using the following average procedure

$$I_p(z) \exp(-p\hbar\omega_0/2kT) \rho(p\hbar\omega_0) \simeq \frac{1}{\hbar\omega_0} \int_{(p-1/2)\hbar\omega_0}^{(p+1/2)\hbar\omega_0} d(\Delta E) I_{\Delta E/\hbar\omega_0}(z) \exp(-\Delta E/2kT) \rho(\Delta E),$$

we have an approximate formula:

$$\bar{W} = \int \bar{W}(\Delta E) \rho(\Delta E) d(\Delta E), \quad (22)$$

where $\bar{W}(\Delta E)$ is defined by

$$\bar{W}(\Delta E) = \frac{2\pi}{\hbar} |M|^2 \frac{1}{\hbar\omega_0} \exp \{-S(2N_0+1)\} I_{\Delta E/\hbar\omega_0}(2S\sqrt{N_0(N_0+1)}) \exp(-\Delta E/2kT), \quad (23)$$

and it corresponds to the average of $W(\Delta E)$ in the energy interval $\hbar\omega_0$. We see that Eq. (23) is identical with Eq. (45) in the previous paper I in the limit of $\Delta E = 0$. Next, in the case of $kT \gg \hbar\omega_0$, $W(\Delta E)$ in (23) is further reduced to

$$\bar{W}(\Delta E) = \frac{2\pi}{\hbar} \frac{|M|^2}{\sqrt{S\hbar\omega_0 kT}} \exp \left\{ - \left(\frac{S\hbar\omega_0}{4} + \frac{\Delta E}{2} \right) / kT \right\}. \quad (24)$$

For a further reduction, the explicit knowledge of $\rho(\Delta E)$ is necessary. If we assume that

$$\rho(\Delta E) = \rho(0) \left(\frac{\Delta E}{kT} \right) / [1 - \exp(-\Delta E/kT)],$$

then we have:

$$\bar{W} = \pi kT \rho(0) \bar{W}(0). \quad (25)$$

Or, if we assume that most of the final states are in the energy interval $-kT \lesssim \Delta E \lesssim kT$, then we have

$$\bar{W} \approx \bar{W}(0). \quad (26)$$

By assuming the spatial uniformity of the fluctuation of the potential, we have an expression of the mobility:

$$\mu = ea^2 \bar{W}/kT. \quad (27)$$

§ 4. Transition Probability (Adiabatic Case)

Here we start from the following Hamiltonian $H_a(\mathbf{X})$

$$H_a(\mathbf{X}) = H - \sum_n K_n \quad (28)$$

where H has been defined by (1). In order to investigate the properties of H_a it is convenient to discuss the relation between H_a and $H^{(m)}$ mentioned in the previous sections. The eigenvalue of the latter, which we denote as $E^{(m)}(\mathbf{X})^*$ is a function of the lattice configuration ($\mathbf{X}$) and has its minimum value at the configuration $(\mathbf{X}_0^{(m)})$. Its eigenstate is denoted as $\phi_m(\mathbf{r}; \mathbf{X})$, where ($\mathbf{X}$) is regarded as a parameter. Then, the function $E^{(m)}(\mathbf{X})$ draws a energy surface in the $3N$ -dimensional space, and a set of the Hamiltonians $(H^{(1)}(\mathbf{X}), \dots, H^{(N)}(\mathbf{X}))$ corresponds to a set of the N energy surfaces $E^{(i)}(\mathbf{X})$ and the N eigenstates $\phi_i(\mathbf{r}; \mathbf{X})$. We illustrate this situation schematically in Fig. 1. Now, let us proceed to the Hamiltonian H_a . We expand the eigenstates of H_a with the eigenstates of the Hamiltonian $H^{(m)}(\mathbf{X})$:

$$\Psi_\mu(\vec{r}; \mathbf{X}) = \sum_m a(\mu, m; \mathbf{X}) \phi_m(\vec{r}; \mathbf{X}), \quad (29)$$

where the coefficients $a(\mu, m; \mathbf{X})$ and the eigenvalues $\epsilon_\mu(\mathbf{X})$ are determined by:

$$\sum_n a(\mu, n; \mathbf{X}) \{H_a m, n; \mathbf{X} - S(m, n; \mathbf{X}) \epsilon_\mu(\mathbf{X})\} = \epsilon_\mu(\mathbf{X}) a(\mu, m; \mathbf{X}). \quad (30)$$

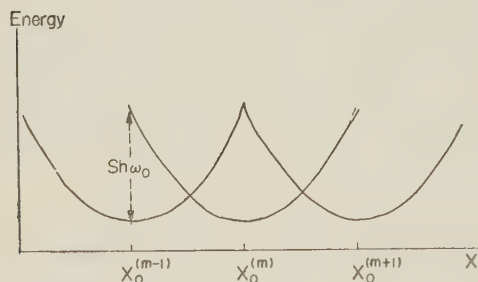


Fig. 1.

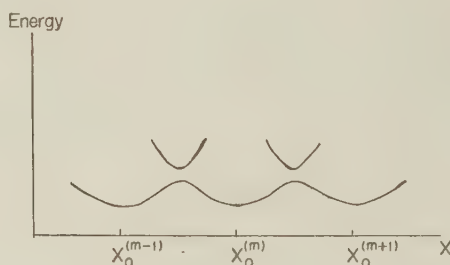


Fig. 2.

Here

$$H_a(m, m; \mathbf{X}) = E^{(m)}(\mathbf{X}), \quad (31)$$

$$H_a(m, n; \mathbf{X}) = (\phi_m(\vec{r}; \mathbf{X}) | \Delta H | \phi_n(\vec{r}; \mathbf{X})) \quad (m \neq n) \quad (32)$$

and

$$S(m, n; \mathbf{X}) = (\phi_m(\vec{r}; \mathbf{X}) | \phi_n(\vec{r}; \mathbf{X})) - \delta_{m,n}. \quad (33)$$

Here we assume that the intensity of the electron-lattice interaction is sufficiently strong and the overlap between ϕ_m and ϕ_n is quite small. Then, it may be plausible to assume that the lowest energy surface and the corresponding wave function are approximated by:

* For the sake of simplicity we denote a set of coordinates

$(\vec{X}_1, \dots, \vec{X}_N)$ by $(\mathbf{X})$ and $(\vec{X}_{10}^{(m)}, \dots, \vec{X}_{N0}^{(m)})$ by $(\mathbf{X}_0^{(m)})$.

$$\epsilon_0(\mathbf{X}) \approx E^{(m)}(\mathbf{X})$$

and

$$\Psi_0(\vec{r}; \mathbf{X}) \approx \phi_m(\vec{r}; \mathbf{X}),$$

when the configuration $(\mathbf{X})$ is close to $(\mathbf{X}_0^{(m)})$. On the other hand, if the two energy surfaces $E^{(m)}(\mathbf{X})$ and $E^{(m+1)}(\mathbf{X})$ intersect,—this situation is realized when $(\mathbf{X})$ is near $\frac{1}{2}(\mathbf{X}_0^{(m)} + \mathbf{X}_0^{(m+1)})$ —, they repel each other owing to the perturbation ΔH . Thus, we may illustrate the energy surfaces $\epsilon(\mathbf{X})$ schematically in Fig. 2.

First, let us discuss the problem by the classical picture, because the classical treatment is familiar in the case of the adiabatic transition. In this picture the motion of the system is represented by that of a representative point in the $3N$ dimensional space whose potential is schematically illustrated in Fig. 2. If the hills between the basins about $(\mathbf{X}_0^{(m)})$ are higher than kT , the representative point oscillates many times about $(\mathbf{X}_0^{(m)})$ and jumps occasionally to one of the nearest basins, say $(\mathbf{X}_0^{(m+1)})$, over the hills. Since the motion of the hole follows adiabatically to the motion of the ions, we need only to consider the transition probability of the ionic configuration from $(\mathbf{X}_0^{(m)})$ to $(\mathbf{X}_0^{(m+1)})$ in order to investigate the transition probability of the hole from the m -th ion to the $(m+1)$ -th ion. The jumping frequency may be given by

$$W = \nu_0 \exp(-\epsilon_h/kT) \quad (34)$$

where ν_0 is the average frequency of the representative point along the direction of $(\mathbf{X}_0^{(m+1)} - \mathbf{X}_0^{(m)})$, and will be the order of the frequency of the lattice vibration and ϵ_h is the height of the hill measured from the bottom of the m -th basin. The value of ϵ_h is approximately estimated by

$$\epsilon_h = \frac{S\hbar\omega_0}{4} + \frac{\Delta E}{2}. \quad (35)$$

In the quantum mechanical treatment the unperturbed Hamiltonian is $H^{(m)}(\mathbf{X}) + \sum K_n$ and the perturbation which causes the transition will be $(\epsilon_0(\mathbf{X}) - H^{(m)}(\mathbf{X}))$. Then, the matrix element of the transition is given by:

$$\sum_{N'_n} \sum_{N''_n} (\Pi \Phi_{n, N'_n}(m) | \epsilon_0(\mathbf{X}) - H^{(m)}(\mathbf{X}) | \Pi \Phi_{n, N''_n}(m+1)). \quad (36)$$

Since it is rather difficult task to evaluate this matrix element, we make a simplified approximation:

$$(\dots | \epsilon_0(\mathbf{X}) - H^{(m)}(\mathbf{X}) | \dots) \rightarrow \bar{M} (\Pi \Phi_{n, N'_n}(m) | \Pi \Phi_{n, N''_n}(m+1)), \quad (37)$$

where $\bar{M}$ is an average value of $(\epsilon_0(\mathbf{X}) - H^{(m)}(\mathbf{X}))$. By this approximation the transition probability $\bar{W}$ takes the same form as in the case of the non-adiabatic approximation. The only difference is the physical meaning of the matrix element $\bar{M}$.

The wave function $\Psi_0(\vec{r}; \mathbf{X})$ changes abruptly its character from ϕ_m -type of ϕ_{m+1} -type at the middle region between $\mathbf{X}_0^{(m)}$ and $\mathbf{X}_0^{(m+1)}$. If the matrix element $H_c(m, m+1; \mathbf{X})$ is quite small, the motion of the electron cannot follow such a sharp change. In this case the adiabatic approximation is not permissible. As is well known, the rough criterion for the adiabatic process says that, if $M > \hbar\omega_0$, the process is regarded as adiabatic. Here M is defined by (8): $M = H_c(m, m+1; \mathbf{X})$.

§ 5. Comparison of Theory with Experiments

The Heitler-London approach we have developed is an idealization of complicated real situations. At present it is not quite certain

how this approach is useful, but we suppose that the H-L approach seems to be adequate in the following examples.

(A) NiO⁵⁾

The NiO crystal may be a typical example

to which the H-L theory of the conductivity is applicable. The conductivity of specimens ($\text{Li}_x\text{Ni}_{1-x}\text{O}$) is observed over a wide range of Li-concentration (x). This material is a semiconductor and both the absolute value and the temperature dependence of the conductivity depend sensitively upon x . In the range of x from 0.1 to 0.01 the conductivity at room temperature is roughly proportional to x , and outside of the above mentioned region the conductivity decreases more rapidly than linear with decreasing concentration. The activation energy δE , which is defined by $\sigma \propto \exp(-\delta E/kT)$, is of the order of 0.1 eV when x is about 0.1, but it amounts to about 1.0 eV when the specimen becomes sufficiently pure. We may interpret this concentration dependence in the following way. When the density of holes, or that of Li^+ ions, is high, a hole which is at one of the nearest neighbours of a Li^+ ion can transfer directly to another position which is again one of the nearest neighbours of another Li^+ ion with nearly the same energy. In this case we can not distinguish between bound and free holes, because every hole contributes almost equally to the current. This is the reason why the conductivity is roughly proportional to the Li-concentration. On the other hand, when the concentration of Li^+ ions becomes smaller, the number of possible paths via nearest neighbours decreases, so that the conductivity decreases more rapidly than linear. Further, when the density of the Ni^{3+} ions is quite small, the most of the holes are bound to the vicinity of Li^+ ions or Ni^{++} vacancies, so that it needs energy of the order of 1 eV to activate a hole to nearly free states. In this case the number of movable holes is given by a similar formula as that in usual semiconductors.

According to Morin's experiment a specimen which is represented by $\text{Li}_{0.1}\text{Ni}_{0.9}\text{O}$ has the following value of the mobility: about 10^{-3} at 300°K , 2×10^{-2} at 500°K and 7×10^{-2} at 1000°K . Here the unit of the mobility is $\text{cm}^2/\text{volt sec}$. Since the Néel temperature of NiO is about 500°K and the characteristic temperature of the longitudinal optical vibrations $\Theta = \hbar\omega_0/K$ is about 880°K , we may use Eq. (26) and Eq. (27) to estimate the transition probability $\bar{W}$ from the observed mobility at 1000°K . The estimated value of

$\bar{W}$ is: $\bar{W} \sim 4 \times 10^{12} \text{ sec}^{-1}$. On the other hand, the frequency of the longitudinal mode of vibration is estimated as: $\nu_0 \simeq 1.8 \pm 10^{13} \text{ sec}^{-1}$. Therefore, we see that the condition $\nu_0 > \bar{W}$ is satisfied in NiO even at high temperature. Since Eq. (24) contains two parameters S and M , we obtain from experiments only a relation between them. The result of the analysis is shown in Table I. We find that the

Table I.

S	$M/\hbar\omega_0$
3	0.14
5	0.20
7	0.27
10	0.41

value of $M/\hbar\omega_0$ is always smaller than unity in a reasonable range of S , so that the non-adiabatic approximation may be applicable to NiO . Next, let us study the temperature dependence of the mobility. Here the situation is rather complicated because of the following reasons. (1)* Since the NiO crystal is an antiferromagnetic substance, we expect that the transition probability W depends upon spin order of the lattice through the matrix element M , and (2) We have no knowledge about $\rho(4E)$. However, these are not serious at high temperature. After some calculations we find from (24) that the temperature dependence of the observed mobility above room temperature is approximately reproduced by the assumption: $S=10$. This value of S may be regarded as an upper limit, because we have disregarded other factors which contribute to the temperature change of the mobility. In fact, the spin-dependence of M might reduce the value of S . Therefore, even when we take into account the approximate nature of the analysis, it may be safe to say that the value of the matrix element M is of the order of $(0.1-0.4) \hbar\omega_0$. On the other hand, the theoretical value of the mobility at 100°K which is

* Morin's experiment shows no trace of the change of the mobility at the Néel temperature, while Yamaka has observed that the conductivity-temperature curve shows a knick at the Néel temperature.

estimated from (24) with the assumption $S=10$ is about one hundred times larger than the observed value. This discrepancy may come from the two reasons: (1) the effect of the antiparallel spin arrangement, or (2) the effect of $\rho(\Delta E)$. Unfortunately the theory developed here is too crude to treat the problem in detail.

(B) LaMnO_3

Zener⁶⁾ has proposed a fascinating idea of the double exchange interaction by which ferromagnetism and conductivity of ($\text{LaMnO}_3 + \text{SrMnO}_3$) are correlated intimately. However, later development of theories and experiments⁷⁾ reveals that the magnetic and electrical properties of LaMnO_3 are not so simple as supposed to be at the first stage of the research. Some of the objections to Zener's original idea are: (1) Anderson and Hasegawa⁸⁾ show that the susceptibility-temperature characteristic which is expected from the double exchange mechanism does not agree with observations. (2) We know that the double exchange mechanism is not indispensable to understand the ferromagnetic interaction in ($\text{LaMnO}_3 + \text{SrMnO}_3$). Other mechanisms of superexchange interaction⁹⁾ can also explain why the interaction in a chain $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ works ferromagnetically. (3) Zener's explanation of the electrical conduction in ($\text{LaMnO}_3 + \text{SrMnO}_3$) is not necessarily unique. According to him the electron transfer is not accompanied with a phonon process. We, however, have proposed in the paper I that another transfer mechanism which is accompanied with phonons can also give a qualitative explanation of the observation. Although Zener's original idea is brilliant, we should not take it too literally.

First, we want to investigate a state of a hole in LaMnO_3 . Let us consider a Mn^{4+} ion and a Mn^{3+} ion which are situated at the π -direction separated by an O^{2-} ion. We denote such a configuration as the π -configuration and choose this direction as a z -axis. Hitherto, we have considered that hole which is localized around an ion. This assumption may be reasonable for the hole in NiO , but not necessarily good for the hole in LaMnO_3 , because the interaction between the 3d electrons of adjacent ions through the intermediate O^{2-} ion is not very small in LaMnO_3 .

Therefore, it may be a better approximation to suppose that the wave function of the hole in a π -configuration is represented by a linear combination of a γ -orbit of the A ion and that of the B ion:

$$\Psi_{AB} = a\psi_A + b\psi_B \quad (a^2 + b^2 = 1),$$

where ψ_A and ψ_B are the wave function of 3d γ -electron in the ions A and B with the same spin state. The wave functions ψ_A , ψ_B and Ψ_{AB} correspond to ψ_m , ψ_{m+1} and Ψ_0 in §4, respectively. Here, we do not postulate from the beginning that $a^2 = b^2 = \frac{1}{2}$ as Zener did, but we shall determine them from the energy consideration. We assume that the wave function ψ_A and ψ_B are determined by the wave equations:

$$\begin{aligned} \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_A(\vec{r}) \right\} \psi_A(\vec{r}; X) &= E^{(A)}(X) \psi_A(\vec{r}; X) \\ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_B(\vec{r}) \right\} \psi_B(\vec{r}; X) &= E^{(B)}(X) \psi_B(\vec{r}; X) \end{aligned}$$

where $U_A(\vec{r})$ and $U_B(\vec{r})$ are the crystal potentials around the ions A and B . Since they are somewhat different owing to the term $\Delta U(\vec{r})$ mentioned in the previous section, the energies $E^{(A)}$ and $E^{(B)}$ are not always equal. Moreover, the state of polarization around the hole depends upon the wave function of the hole itself,* so that we expect that the energy of the system depends upon a and b . However, we note that, whatever the exact value of b may be, the total energy of the system in the π -configuration becomes lower owing to this type of mutual interaction, if the spin orientation of the both ions is the same. Therefore, we find that this type of the interaction is ferromagnetic, and we can estimate the upper limit of b from the knowledge of the Neel temperature, if we assume tentatively that the ferromagnetic interaction in LaMnO_3 comes solely from this origin.

A simple computation shows that the energy gain due to the spreading of the wave function and the probability amplitude of the spreading are given by:

$$J' = \varepsilon_0 - E^{(A)} = -M^2 / [(E^{(B)} - E^{(A)}) + I],$$

* The polarization energy becomes largest when $a^2=1$ and $b=0$, if the wave functions ψ_A and ψ_B are well localized around each nucleus.

and

$$b = -M/[(E^{(B)} - E^{(A)}) + I] .$$

Here M is the transition matrix element defined by (8) and I comes from the change of the polarization energy and its magnitude is the order of $S\hbar\omega_0$. We shall estimate the order of the magnitude of J' and b in the following way. As to M we expect that it is larger than that in NiO, because we treat here the transition of the $d\gamma$ -electron in contrast with the ds -electron in NiO. Therefore, we assume tentatively that $M \sim 0.05$ eV. The specimen $(\text{La})_{0.7}(\text{Sr})_{0.3}\text{MnO}_3$ has the Curie temperature at 370°K , so that the magnitude of J_{ex} estimated from the well-known relation

$$kT_c = \frac{2}{3} J_{ex} Z(S_0 + 1)S_0(0.3) \quad (Z=6, S_0=2)$$

is of 6×10^{-3} ev. If we put J_{ex} equal to J , then the value of b is estimated as about 0.1. Although the method of estimation is very crude,* we see that the value of b^2 is much smaller than a^2 , and small amount of the modification of the original atomic function is sufficient to interpret the observed ferromagnetic coupling in LaMnO_3 .**

Next, let us investigate mechanism of the conduction by using the adiabatic approximation. Since the states $(a\psi_A + b\psi_B)$ and $(b\psi_A + a\psi_B)$ correspond to different configuration of the lattice, we can imagine a transfer between these configurations. The matrix element concerning this transfer is not M , but $\bar{M}$ defined by (37). We note that this process has nothing to do with ferromagnetism and the ferromagnetic interaction is concerned with the nature of the electronic wave function $(a\psi_A + b\psi_B)$, but not with the state of the lattice configuration. The transition of the hole mentioned before however, does not contribute to the observable current as long as the density of the Sr^{++} ions is very small and the motion of the hole is con-

fined to the very vicinity of the separated Sr^{++} ions. In this case some amount of the activation energy is necessary to liberate the holes from the potential valley, so that the conductivity is expected to be semiconductor-like. When the density of the Sr^{++} ions becomes as large as 0.2~0.4, the situation seems to be similar to the case of $\text{Ni}_{1-x}\text{Li}_x\text{O}$ with $x \simeq 0.1$. According to the experiment the conductivity increases by a large amount between the concentration of the Sr^{++} ions 0.1 and 0.2. In this region of concentration the temperature dependence of the conductivity shows a remarkable change from semiconductor-like to metallic with increasing concentration. Next, let us analyze the observed current in the specimen $(\text{La})_{0.7}(\text{Sr})_{0.3}\text{MnO}_3$. It shows the metallic conductivity and its mobility is estimated as $0.2 \text{ cm}^2/\text{volt sec}$ at room temperature. As mentioned previously the matrix element M is expected to be larger than $\hbar\omega_0$, so that the adiabatic approximation seems to be better for this case. If we take $S=3$ in (23) so as to give a metallic temperature dependence of the conductivity, the value of the perturbation matrix $\bar{M}$ is found to be nearly equal to $\hbar\omega_0$. Therefore, the order of magnitude of the parameters seems to be reasonable.

(C) Magnetite¹⁰⁾

Magnetite may be another example whose current is interpreted by the H-L concept of the conductivity. According to experiments the conductivity of magnetite is nearly constant at high temperature and its magnitude is about $200 (\text{ohm-cm})^{-1}$. Since both types of iron ions, Fe^{3+} and Fe^{2+} , distribute at random on its sixteen sites, we expect that the number of the conduction electrons is equal to the number of the Fe^{2+} ions. If so, we see that the mobility of the conduction electron is much smaller than one $\text{cm}^2/\text{volt sec}$ even at high temperature. We suppose that the conduction mechanism in magnetite at high temperature is similar to that of $(\text{LaMnO}_3 + \text{SrMnO}_3)$ when the concentration of the Sr^{++} ions is sufficiently large. A situation is more complicated below the critical temperature. The ions Fe^{3+} and Fe^{2+} make a more or less ordered arrangement, so that there is the potential difference between the positions which are mainly occupied by Fe^{3+} ions and those by Fe^{2+} ions. In the wandering mo-

* We believe that there exist other types of ferromagnetic interaction in LaMnO_3 , so that the above estimated value of b may be larger than the real value.

** In this type of the ferromagnetic interaction the state with parallel spin configuration is always lower than that with antiparallel spin configuration so that there is no difficulty concerning the interpretation of the observed susceptibility. This difficulty was pointed out by Anderson and Hasegawa⁸⁾ as a fault of the double exchange mechanism.

tion of the electrons, the electrons must climb up and down the potential hills. The total rate of the wandering motion may be determined by the climbing-up process, because it takes a much shorter time for electrons to go down the hill. The simple theory developed in the previous sections is insufficient to treat this complicated phenomenon in detail, but we shall discuss it qualitatively by the aid of the formula (20). We expect that the distribution of $\rho(\Delta E)$ displaces towards a larger value of p below the transition temperature owing to the increased potential difference. Then, the transition probability $\bar{W}$ becomes much smaller, because it contains the functions $\exp(-p\hbar\omega_0/2kT)$ and $I_p(x)$. The slope of $\log(\text{conductivity})$ vs $1/T$ curve is also determined by the distribution of these functions in (20). Therefore, we see easily that the mobility becomes smaller when the slope of $\log(\text{conductivity})$ vs $1/T$ curve is steeper. This general tendency seems to be recognized by observations.

(D) CoFe_2O_4

Recently Jonker¹¹⁾ investigated the semi-conducting properties of a series of mixed crystals $\text{Co}_{3-x}\text{Fe}_x\text{O}_4$ in the range of x from 1.90 to 2.10. The CoFe_2O_4 crystal has the inverse spinel structure. One-half of the trivalent iron ions are on tetragonal sites, while the rest of them and the divalent cobalt ions are on octahedral sites. When x is larger than 2, the excess iron ions are regarded as divalent. On the contrary, when x is less than 2, the excess cobalt ions are regarded as trivalent. It is a very interesting point of Jonker's experiment that we can control the valency of the ions without introducing impurity ions. Thus, we may assume that the number of electrons contributing to the conductivity is equal to the number of the divalent iron ions. The situation is similar in the case of holes. According to Jonker the mobility of electrons (or holes) is quite small as compared with one $\text{cm}^2/\text{volt sec}$, and it increases exponentially with increasing temperature. He assumes that the mobility is given by:

$$\mu_i = \frac{ea^2}{kT} \nu_i \exp(-q_i/kT)$$

($i=1$ for electrons and $i=2$ for holes). Here a is the distance between neighbour octahed-

ral sites, q is the activation energy and ν is the lattice frequency active in the jumping process. In the range of x from 1.90 to 2.10 these constants are determined as follows: $\mu_1 = 0.7 - 1.3 \times 10^{-4} \text{ cm}^2/\text{volt sec}$, $\mu_1/\mu_2 = 10^4$ at room temperature, $q_1 = 0.205 - 0.175 \text{ eV}^*$ and $\nu_1 = 6.5 \times 10^{12} \text{ sec}^{-1}$.

Let us investigate the reason why the mobility is very small in this crystal. If we compare the behaviour of the electron current in CoFe_2O_4 with that in magnetite, we see easily that the nature of the current in CoFe_2O_4 is quite similar to that in magnetite below the transition temperature. Therefore, we suppose that the conduction mechanism CoFe_2O_4 is similar to that in magnetite at low temperature. There may be rather large fluctuations of the potential in the CoFe_2O_4 lattice, so that the motion of the electrons is much reduced by the potential fluctuations and it becomes highly temperature dependent.**

(E) Impurity Conduction

As is well known, the impurity conduction in semiconductors will be band-type at high concentration of the impurity atoms, while it is H-L type at low concentration.¹²⁾ In the latter case the characteristic features are: (1) The correction effect between electrons is so important that the conduction is only possible with some degree of compensation. (2) The transfer integral M between different impurity atoms is pretty small as compared with the amount of the potential fluctuation. Then, the diffusion of electrons is possible only when the condition of the energy conservation is satisfied through cooperation of

* The temperature dependence of the current comes from two factors, that is, the potential fluctuation and the electron-lattice interaction. In (20) they are given by $\exp(-p\hbar\omega_0/2kT)$ and $I_p(x) \times \exp\{-S(2N_0+1)\}$, respectively. The observed activation energy of about 0.2 eV is too large to ascribe it to the electron-lattice interaction.

** Since the density of electrons is large, we cannot divide the excess electrons into two groups; electrons which are bound to the excess ions and activated nearly free electrons. However, the concentration is still a little too small to smooth out the potential fluctuation. In this respect, the situation in CoFe_2O_4 is similar to that in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ when x is slightly smaller than 0.1. According to the experiments the behaviours of the current in both cases are similar.

phonon processes. In contrast with the preceding examples, the electron-lattice interaction is rather weak, so that one phonon process is dominant, especially in germanium. Since the energy conservation is satisfied by the aid of the phonon process, the transition

probability becomes large with increasing intensity of the interaction. The transition probability is obtained by the similar procedure as mentioned in the preceding sections. We describe details of the derivation in Appendix II and mention only a result here:

$$W(\Delta E) = A \left\{ \frac{N(q_0)}{N(q_0)+1} \right\} \cdot \frac{4}{9\pi} \frac{1}{\hbar} \frac{C^2 |M|^2}{m_0 c^2 (\Delta E)^2} V q_0^3, \quad \text{for } \begin{cases} \Delta E > 0, \\ \Delta E < 0, \end{cases} \quad (38)$$

where C is the interaction constant between electrons and longitudinal acoustic phonons, m_0 is the mass per unit cell, V is the volume of the unit cell, c is the sound velocity, $N(q_0)$ and q_0 are defined as:

$$N(q_0) = 1 / [\exp(|\Delta E|/kT) - 1], \quad (39)$$

and

$$\hbar c q_0 = |\Delta E|. \quad (40)$$

If we adopt the Hydrogen-like wave function for the impurity state, the expression (38) is reduced to

$$W(\Delta E) = 16A \frac{\xi |M|^2 \Delta E}{\hbar (\hbar c/R)^2} [\exp(\Delta E/kT) - 1]^{-1}, \quad (41)$$

where R is the Bohr radius of the impurity state, ξ is the difference between the optical and thermal ionization energies of the impurity state due to the electron-lattice interaction:

$$\xi = \frac{1}{36\pi} \frac{V}{R^3} \frac{C^2}{m_0 c^2}. \quad (42)$$

Finally, A is a factor which corresponds to $\exp(-S(2N_0+1))$ in the cases of the polar crystal, and it is a somewhat complicated function of temperature. When T is zero, it is given by:

$$A = \exp \left\{ -\frac{16}{3\pi} \frac{\xi}{\hbar c/R} \right\}. \quad (43)$$

By the analysis of experiments the values of these constants are estimated as: $C \sim 7.5$ eV and $R \sim 50$ Å in germanium; $C \sim 40$ eV and $R \sim 25$ Å in silicon. Then, we have: $\xi \sim 0.09$ k and $\hbar c/R \sim 8$ k in germanium, and $\xi \sim 17$ k and $\hbar c/R \sim 25$ k in silicon, respectively. For the purpose of a detailed comparison with experiments we assume:

$$\rho(\Delta E) = \rho(0) \left(\frac{\Delta E}{kT} \right) / [1 - \exp(-\Delta E/kT)]$$

and then we have:

$$\bar{W} = \int_{-\infty}^{\infty} W(\Delta E) \rho(\Delta E) d(\Delta E) = \frac{32\pi^2 A}{3} \frac{\xi \rho(0) (kT)^2 |M(d)|^2}{\hbar (\hbar c/R)^3}, \quad (44)$$

and

$$\sigma = ne\mu = ne^2 d^2 \bar{W} / kT. \quad (45)$$

Here n is the number of carriers which participate the impurity conduction, d is the average distance between nearest neighbour impurity atoms, and $M(d)$ is the value of the matrix M in that distance. As to the number n the situation is rather complicated. When the density of the impurity atoms is very small, the number of movable carriers is limited by $N_{\min}$

(the number of the minority atoms). Moreover, the greater part of these carriers are trapped in the vicinity of the charged minorities, because the observation is carried out at very low temperature. In this case it may be allowed to divide the carriers into two parts; conductive carriers and bound carriers. The conductive carriers wander through the lattice surmounting the fluctuation of the potential. Then, we assume:

$$n = N_{\min} \exp(-q/kT) \quad (46)$$

although this assumption is not quite convincing.

Now, let us study the matrix element $M(d)$ as a function of d . By using the observed data of the conductivity in germanium specimens with various contents of impurity, and Eq. (44)~Eq. (46), we obtain a set of values of $M(d)\sqrt{\rho(0)}$, and plot them in a graph.* Here we assume that d is given by

$$d = (3/4\pi N_{\text{maj}})^{1/3}; \quad (N_{\text{maj}}$$

= the number of the majority atoms),

and we take $T = 2.5^\circ\text{K}$ and $\xi = 0.09k$. As to A we may take it as unity, because $(\hbar c/R)$ is always much larger than ξ . On the other hand, we expect that the following theoretical formula concerning $M(d)$ is not far from truth:

$$M(d) = \frac{1}{\pi R^3} \int e^{-|\vec{r}-\vec{R}_A|/R} \frac{e^2}{\kappa|\vec{r}-\vec{R}_B|} e^{-|\vec{r}-\vec{R}_B|/R} d\tau$$

$$\doteq 200k \left(1 + \frac{d}{R}\right) \exp\left(-\frac{d}{R}\right),$$

where $\vec{R}_A$ and $\vec{R}_B$ are the position vectors of the impurity atoms A and B . Thus, we adopt a functional form

$$M(d) = (\text{const.})k(1 + d/R') \exp(-d/R')$$

as an empirical formula, and determine the value of R' so as to give a best fit to observed values $M(d)\sqrt{\rho(0)}$. Then, the best fit is obtained by $R' \sim 43\text{\AA}$ (Fig. 3). This value is compared with the value $R \sim 50\text{\AA}$ which is derived by using the Hydrogen model and another set of experimental values.* Although we have introduced many crude approximations, the result is still reasonable enough to justify the H-L approach to the impurity conduction.

Appendix I.

In this appendix we show that the usual polaron theory is inadequate for describing the state of a hole in Ni^{++} ions in the NiO crystal, and the hole is probably self-trapped by a single Ni^{++} ion for sufficiently long time as compared with a period of the optical lattice vibration. Let us consider an extra positive hole in an otherwise perfect lattice consisting of ions with a closed shell structure. We describe the Hamiltonian of the system as:

$$H = \frac{p^2}{2m} + \sum_n U(\vec{r} - \vec{X}_n) + V(\vec{X}_1 \cdots \vec{X}_N) + \sum_{n=1}^N K_n. \quad (\text{A-16})$$

* As to q we use the observed values.

** Further, if we want to fit the value of (const.) with the theoretical value 200, we need to take $\rho(0) \sim (20k)^{-1}$, but we cannot put much confidence to this result, because we have introduced an ambiguous assumption (46).

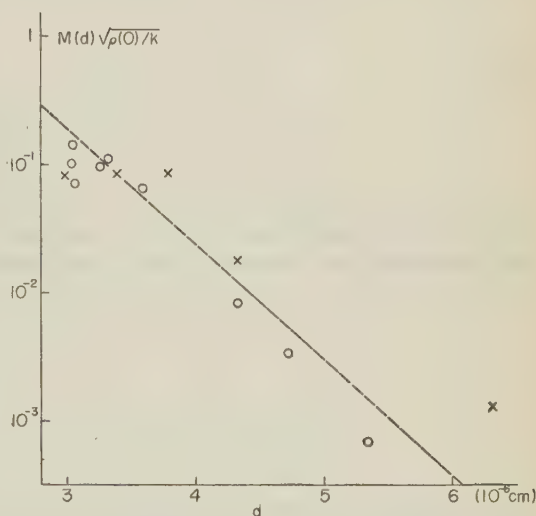


Fig. 3. A relation between the transfer integral and density of the impurity atoms in Ge.

$M(d)\sqrt{\rho(0)}/k$: a quantity proportional to the transfer integral at distance d .

d : an average distance between the nearest neighbour impurities.

○: $n\text{-Ge}$; ×: $p\text{-Ge}$.

The meaning of the terms is given in the section 2. Let us imagine that a hole is bound to a certain ion, say the ion m , then polarization is induced around the ion so as to make the total energy minimum. We have denoted this minimum configuration as $(\mathbf{X}_0^{(m)})$. First, we consider the motion of the hole in the configuration $(\mathbf{X}_0^{(m)})$. Then, the wave equation is given by:

$$\left\{ \frac{p^2}{2m} + eU(\vec{r} - \vec{R}_m) + e \sum_{n \neq m} U(\vec{r} - \vec{X}_{n0}^{(m)}) \right\} \psi = E\psi.$$

This equation is rewritten as:

$$\begin{aligned} & \left\{ \frac{p^2}{2m} + eU(\vec{r} - \vec{R}_m) + e \sum_{n \neq m} [U(\vec{r} - \vec{X}_{n0}^{(m)}) - U(\vec{R}_m - \vec{X}_{n0}^{(m)})] \right\} \psi \\ & = \{E - e \sum_{n \neq m} U(\vec{R}_m - \vec{X}_{n0}^{(m)})\} \psi, \end{aligned}$$

where

$$e \sum_{n \neq m} U(\vec{R}_m - \vec{X}_{n0}^{(m)}) = e \sum_{n \neq m} U(\vec{R}_m - \vec{R}_n) + \sum_{n \neq m} P(\vec{R}_m - \vec{X}_{n0}^{(m)}) \quad (\text{A-17})$$

is the potential energy of the hole at the center of the ion m , and it consists of the electrostatic potential energy in the normal lattice and the potential energy due to the polarization of the medium. Next, we consider the expectation value of (A-16):

$$\begin{aligned} \langle H \rangle &= \left\langle \frac{p^2}{2m} + eU(\vec{r} - \vec{R}_m) + e \sum_{n \neq m} [U(\vec{r} - \vec{X}_{n0}^{(m)}) - U(\vec{R}_m - \vec{X}_{n0}^{(m)})] \right\rangle \\ &+ \langle e \sum_{n \neq m} U(\vec{R}_m - \vec{X}_{n0}^{(m)}) \rangle + \langle V(\vec{X}_0^{(m)}) \rangle + \langle e \sum_n [U(\vec{r} - \vec{X}_n) - U(\vec{r} - \vec{X}_{n0}^{(m)})] \rangle \\ &+ \langle \sum_n [K_n + V(\mathbf{X}) - V(\mathbf{X}_0^{(m)})] \rangle. \end{aligned} \quad (\text{A-18})$$

The problem is to determine the equilibrium positions of the ions together with the electronic state of the hole. In general, this problem is rather complicated. However, if the wave function of the hole is well localized within a small volume as compared with the lattice distance, we may easily compute the induced dipoles in the lattice through replacing the continuum distribution of the extra charge by a point charge e at the center of the ion m . In fact, the wave function of the electron overlaps some extent with the wave function of nearest neighbour ions, so that we must take into account exchange interaction and overlap interaction together with the electrostatic interaction. However, our approach corresponds to the crystalline field approximation which is usually adopted in the theory of magnetism. Under this approximation the expectation value of the first term in (A-18) is E_0 , that is, the ground state energy of the hole in a free nickel ion, the interpretation of the second term is given by (A-17) and the expectation value of $V(\mathbf{X}_0^{(m)})$ plus the second terms is equal to the sum of the Madelung energy of the lattice and $-1/2 \sum_{n \neq m} P(\vec{R}_m - \vec{X}_{n0}^{(m)})$, because the lattice is in equilibrium at $(\mathbf{X}_0^{(m)})$. Further, we assume that the expectation value of the fourth term is negligibly small. In treating the last term we assume that the deviation $\mathbf{X} - \mathbf{X}_0^{(m)}$ is quite small and the motion of the ions is approximately represented by a set of the harmonic vibrations with a suitable set of normal coordinates. Then, the expectation value of the last term is given by: $\sum_n \hbar \omega_n$. In order to estimate the polarization energy we adopt the Mott-Littleton approximation. Then, the potential energy due to the polarization around a point charge e is given by:

$$V = -\frac{e}{a} [6.3346M_2 + 10.1977M_1],$$

where a is the nearest neighbour distance, and M_1 and M_2 are given by:

$$M_1 = (2/4\pi) \left(1 - \frac{1}{K} \right) (\alpha_1 + p_a) / [2p_a + \alpha_1 + \alpha_2] ,$$

$$M_2 = (2/4\pi) \left(1 - \frac{1}{K} \right) (\alpha_2 + p_a) / [2p_a + \alpha_1 + \alpha_2] .$$

Here α_1 , α_2 , $2p_a$ and K are the polarizability of the O^{--} ion, of the Ni^{++} ion, the dipole moment due to the ion displacement ($2Zed$) and the static dielectric constant of the NiO crystal. On the other hand, if we consider only the polarization due to the deformation of the ion cores, the potential energy is given by:

$$V_0 = -\frac{e}{a} [6.3346M_2' + 10.1977M_1']$$

where M_1' and M_2' are defined by:

$$\begin{cases} M_1' = (2/4\pi) \left(1 - \frac{1}{K_0} \right) \alpha_1 / (\alpha_1 + \alpha_2) , \\ M_2' = (2/4\pi) \left(1 - \frac{1}{K_0} \right) \alpha_2 / (\alpha_1 + \alpha_2) . \end{cases}$$

respectively. Here K_0 is the optical dielectric constant. After a simple calculation we obtain the values: $M_1 = 0.1040$, $M_2 = 0.0416$, $M_1' = 0.0594$ and $M_2' = 0.0033$.* Since we disregard the potential energy due to the electronic polarization, the potential energy which we want to have is evaluated from the following equation

$$P = V - V_0$$

and its numerical value is -4.7 ev. Therefore, the total energy of the system is:

$$E_{tot} = E_0 + (\text{electrostatic energy in the normal lattice}) + \frac{1}{2}P; \quad (\frac{1}{2}P = -2.4 \text{ ev}) .$$

On the other hand, if we assume that the positive hole behaves like a polaron, then the energy of the ground state is estimated from the Landau-Pekar approximation. The result is:

$$E_{tot} = E_0 + (\text{electrostatic energy in the normal lattice}) + E(0) + \frac{1}{2}E_{pol}(m^*) .$$

Here $E_{pol}(m^*)$ is defined as:

$$E_{pol}(m^*) = -\left(\frac{1}{10} \right) \alpha^2 \left(\frac{m^*}{m} \right) \hbar \omega_0 ,$$

$$\alpha = \frac{e^2}{2\hbar} \sqrt{\frac{2m}{\hbar \omega_0}} \left(\frac{1}{K_0} - \frac{1}{K} \right) = 1.74$$

where m is the electron mass and m^* is the effective mass of the hole, respectively. Finally, $E(0)$ is the energy of the band edge measured from the energy $E_0 + (\text{electrostatic energy in the normal lattice})$. This term means energy gain due to band formation. Although no reliable computation of the band structure of NiO has been published, it is almost certain that the band width of the each $3d$ band is smaller than 1.0 eV and $E(0)$ is much smaller than 1.0 eV. Since the energy $E_{pol}(m^*)$ is much smaller than 1.0 eV except for a case of extremely heavy mass of the hole, we see that a self-trapped state may be realized in the NiO lattice.

Appendix II.

We shall derive a formula of the transition probability of the impurity conduction. We

* $K=12$, $K_0=5.4$ and $\hbar\omega_0=0.0076$ eV.

take the Hamiltonian of the system as follows:

$$H = H_{el} + H_{ph} + H_{int} + \sum_m V(\vec{r} - \vec{R}_m) + \Delta U(\vec{r}), \quad (\text{A-33})$$

where H_{el} is a sum of the kinetic energy of an electron and the potential energy of the periodic lattice, H_{ph} is the Hamiltonian of the phonon system, H_{int} is that of the electron-phonon interaction, in which only the longitudinal acoustic phonons are considered, $V(\vec{r} - \vec{R}_m)$ is the potential of the m -th impurity atom located at $\vec{R}_m$ and $\Delta U(\vec{r})$ is the fluctuation of the potential mentioned in §2. The Hamiltonians H_{ph} and H_{int} take the usual expressions:

$$H_{ph} = m_0 \sum_{\vec{q}} \omega_{\vec{q}}^2 (a_{\vec{q}} a_{\vec{q}}^* + a_{\vec{q}}^* a_{\vec{q}}) \quad (\text{A-34})$$

and

$$H_{int} = \sqrt{\frac{V}{\Omega}} \cdot \frac{2C}{3} i \sum_{\vec{q}} |q| (a_{\vec{q}}^* \exp(-i\vec{q} \cdot \vec{r}) - a_{\vec{q}} \exp(i\vec{q} \cdot \vec{r})), \quad (\text{A-35})$$

where $\vec{q}$ is the wave number vector of phonon, Ω is the total volume of the system and finally a 's satisfy the condition:

$$a_{\vec{q}} a_{\vec{q}'}^* - a_{\vec{q}'}^* a_{\vec{q}} = \frac{\hbar}{2m_0 \omega_{\vec{q}}} \delta_{\vec{q}\vec{q}'}.$$

Following the procedures mentioned in §2, we consider the Hamiltonian $H^{(m)}$ which is defined as:

$$H^{(m)} = H_{el} + H_{ph} + H_{int} + V(\vec{r} - \vec{R}_m) + \Delta U(\vec{r}). \quad (\text{A-36})$$

Since the effect of H_{int} is sufficiently small as compared with the binding energy of the electron in the impurity atom, and $\Delta U(\vec{r})$ is a slowly varying potential, the eigenfunction ψ_m of $H^{(m)}$ may be approximately given by:

$$\psi_m = \phi(\vec{r} - \vec{R}_m) \prod_{\vec{q}} \phi_{\vec{q}, N_{\vec{q}}}^{(m)}, \quad (\text{A-37})$$

where $\phi(\vec{r} - \vec{R}_m)$ is the eigenfunction of $H_{el} + V(\vec{r} - \vec{R}_m)$ and $\phi_{\vec{q}, N_{\vec{q}}}^{(m)}$ is that of

$$m_0 \omega_{\vec{q}}^2 (a_{\vec{q}} a_{\vec{q}}^* + a_{\vec{q}}^* a_{\vec{q}}) + \sqrt{\frac{V}{\Omega}} \frac{2C}{3} i |q| \times \int \phi^*(\vec{r} - \vec{R}_m) (a_{\vec{q}}^* \exp(-i\vec{q} \cdot \vec{r}) - a_{\vec{q}} \exp(i\vec{q} \cdot \vec{r})) \phi(\vec{r} - \vec{R}_m) d\vec{r}. \quad (\text{A-38})$$

If $\phi(\vec{r} - \vec{R}_m)$ is the Hydrogen-like wave function with a radius R , the second term of (A-38) is reduced to

$$\sqrt{\frac{V}{\Omega}} \frac{2}{3} C i |q| \frac{16}{(4 + q^2 R^2)^2} (a_{\vec{q}}^* \exp(-i\vec{q} \cdot \vec{R}_m) - a_{\vec{q}} \exp(i\vec{q} \cdot \vec{R}_m)). \quad (\text{A-39})$$

The residual part of the Hamiltonian, $\Delta H = H - H^{(m)}$ causes the transition between the states m and m' . The transition probability is calculated by Eq. (7). In the present case, however, the electron-lattice interaction is weak, so that one phonon process is dominant. The results are given by Eq. (38) through Eq. (42). In the derivation we have neglected the terms containing $\cos(\vec{q}(\vec{R}_m - \vec{R}_{m'}))$, because $\vec{q}(\vec{R}_m - \vec{R}_{m'})$ is in general large. Moreover, we have neglected the quantity $\{q_0 \times (\text{the effective radius of } \phi(\vec{r} - \vec{R}_m))\}^2$ as compared with unity.

References

- 1) J. Yamashita and T. Kurosawa: *J. Chem. Phys. Solids* **5** (1958) 34.
- 2) N. F. Mott: *Proc. Phys. Soc. London A*, **62** (1949) 416.
- 3) L. Van Hove: *Physica* **21** (1955) 517; **23** (1957) 441.
- 4) R. Kubo: *Phys. Rev.* **86** (1952) 929. K. Huang and A. Rhys: *Proc. Roy. Soc. A*, **204** (1950) 406. M. Lax: *J. Chem. Phys.* **20** (1952) 1752. R. C. O'Rourke: *Phys. Rev.* **91** (1953) 265. H. D. Vasileff: *Phys. Rev.* **96** (1954) 603.
- 5) F. J. Morin: *Phys. Rev.* **93** (1954) 1199. R. R. Heikes: *Phys. Rev.* **99** (1955) 1232. E. Yamaka and K. Sawamoto: *Phys. Rev.* **112** (1958) 1861.
- 6) C. Zener: *Phys. Rev.* **82** (1951) 403.
- 7) J. B. Goodenough: *Phys. Rev.* **100** (1955) 564.
- 8) P. W. Anderson and H. Hasegawa: *Phys. Rev.* **100** (1955) 675.
- 9) J. Kondo and J. Yamashita to be published in *Progr. Theor. Phys.*
- 10) P. A. Miles, W. B. Westphal and A. von Hippel: *Rev. Mod. Phys.* **29** (1957) 279.
- 11) G. H. Jonker: *J. Chem. Phys. Solids* **9** (1959) 165.
- 12) N. F. Mott: *Canad. J. Phys.* **34** (1956) 1356. E. M. Conwell: *Phys. Rev.* **103** (1956) 51. T. Kasuya: *J. Phys. Soc. Japan* **13** (1958) 1096. T. Kasuya and S. Koide: *J. Phys. Soc. Japan* **13** (1958) 1287.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

Anomalous Growth of MoO_3 Crystals

By Eiji YODA

*Department of Physics, Faculty of Science,
Kyoto University*

(Received December 7, 1959)

The growth of molybdenum trioxide crystals from the vapour phase in air and in oxygen gas was studied optically, and an extraordinary growth mechanism was found. The vapour impinging upon a surface did not crystallize directly, but instead it passed through a liquid state before crystallization. The liquid consists of MoO_3 and MoO_3' , the latter being a new phase probably related to the polymerization of MoO_3 vapour or the liquid structure of MoO_3 . The lattice parameters of MoO_3' were estimated from the X-ray data. The origination and stability of the liquid phase were discussed briefly, and it was ascertained that this crystallization mechanism accelerates remarkably the growth rate of the crystal. Also the anisotropy of surface migration of the vapour molecules adsorbed on the crystal surface was analysed. The migration velocity of adsorbed molecules is about 1.5 times larger in the c -direction than in the a -direction of MoO_3 crystal, and hence the morphology of closed loop steps was accounted for.

Part I

§ 1. Introduction

Molybdenum trioxide has been studied by many investigators^{1), 2)} by use of the electron microscope and electron diffraction methods. In vacuum, both the change in quality and the reduction occur during long irradiation of electron. Many of them, however, have treated mainly the reducing process, but scar-

cely the growing process. Therefore, the present author has observed optically the growing process of crystals in air or in oxygen gas.

It was found that there appeared singular and paired growth spirals of opposite signs on the crystal surfaces when the source temperature was elevated to 900°C ³⁾.

Besides an ordinary growing process, an

extraordinary mechanism was found. Namely, many spots having diameters of $0.5\sim 5\mu$ moved on the crystal surfaces, which later on formed layers of the same breadth as their diameters and the height of $0.01\sim 1\mu$, or in some case they moved onto the growth ends of needle crystals, forming new needles. The observed lower limit of 0.5μ of the diameter was restricted by the resolving power of the optical microscope.

In the present paper will be reported the reason why such a phenomenon takes place, since this process plays an important role in the acceleration of crystal growth, through the increase of thickness of the layer as well as in the formation of new crystals.

It was confirmed that the spots were in liquid state in the growing condition, namely, they were droplets. At room temperature they solidified and gave bright spots under the crossed nicols, and showed very rapid smelting by dilute alkali solution as compared with MoO_3 .

§ 2. Preparation of Crystals

Molybdenum trioxide is usually prepared by thermal decomposition of ammonium molybdate¹⁾, the oxidation of metallic molybdenum²⁾ or commercially by roasting molybdenum sulfide in air. By these methods, however, the production of large single crystals is difficult. In the present work, therefore, the sublimation method from pure MoO_3 powder (99.98%) in air was used in order to avoid the intermixing of impurities, and thus single crystals of 1 cm wide, 2 cm long and 0.1 mm thick were obtained.

MoO_3 has an orthorhombic structure ($b > a > c$)³⁾ and the growing velocity is largest in the direction of the c -axis and smallest along the b -axis, so that the crystal is elongated in the [001] direction and the film surface is parallel to the (010) plane. There are many wide and irregular layers on the surface and the growth of these layers starts usually from

the edges or corners of crystals as in the case of WO_3 ⁵⁾.

The higher the source temperature was elevated, the more the step heights increased, if the growth temperature was held constant.

As shown in Fig. 1, purified MoO_3 powder was settled in a silica tube and was heated by a temperature-gradient electric furnace. The flux velocity of vapour in the tube could be controlled arbitrarily by a leak-cock, and the temperatures of the sample as well as at the growing position were measured by platinum-platinum rhodium thermocouple which was movable freely in the tube. The crystals were grown up at low temperature parts of the tube, and it was ascertained by X-ray diffraction that they were MoO_3 .

§ 3. Observation of Droplet Growth*

By direct observation of the growing crystals with an optical microscope, it was observed that droplets were moving on the crystal surface, afterwards forming layers as shown in Photo. 1 (a), or forming new crystals as seen in (b). Needle crystals were formed in the same manner, too. The melting point of the droplets is considerably lower than that of MoO_3 crystal. They were first formed at the layer steps or border parts of the crystals and then travelled along them, but on a wide surface they travelled along the direction of the c -axis more preferably than along that of the a -axis.

The velocity of movement of the droplets is very much influenced by several factors such as the size of the droplets, the step height of layer left behind them, the growing temperature and the quantity of vapour supplied. The shape of layer is of echelon type, because the ordinary layer formation to the step side occurs simultaneously together with the droplet layer formation. Thus, the ratio of the growing velocities of both types of layer formation could be estimated on the photographs. It was found that the growing velocity due to droplets are usually from 1.5 to 10 times faster than that of the ordinary layer formation. The fact will be discussed later.

Sometimes droplets disappeared when they

* For brevity "Droplet Growth" will be abbreviated as "D.G." in the following unless otherwise mentioned.

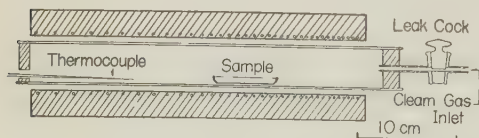
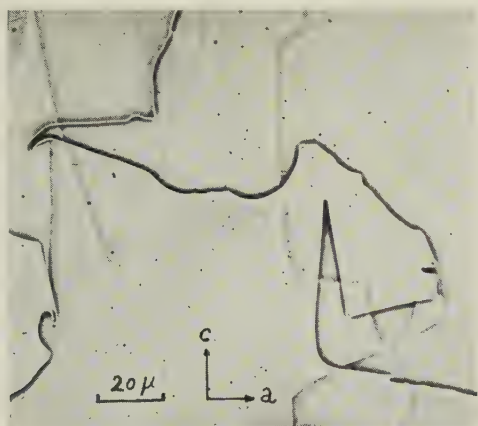
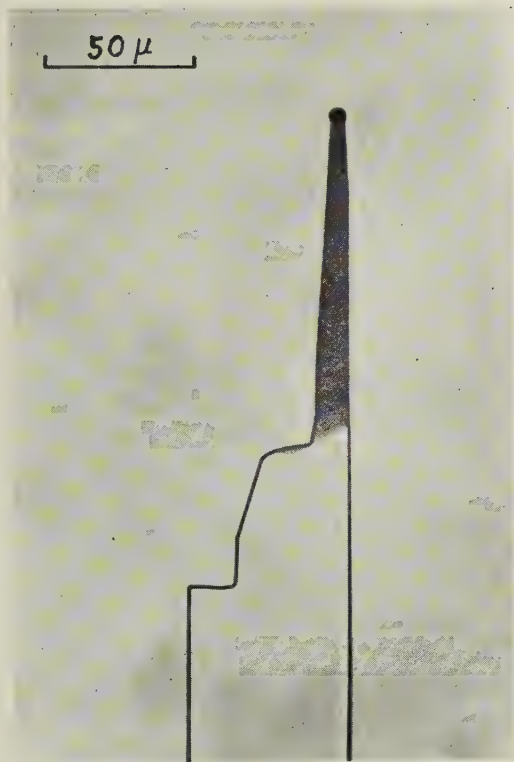


Fig. 1. The construction of temperature-gradient electric furnace.

have arrived, from behind, at the step of the forward-moving layer. And often, apart from the growth ends they individually moved on a surface very rapidly, and when they were originated on the side plane (100) of a crystal, they repeated rapid going- and returning-



(a)



(b)

Photo. 1. (a) Origination of droplets from the step side and layer formation on the (010) plane of MoO_3 .

(b) Formation of new needle-shape crystals. Coloration of this part is due to interference.

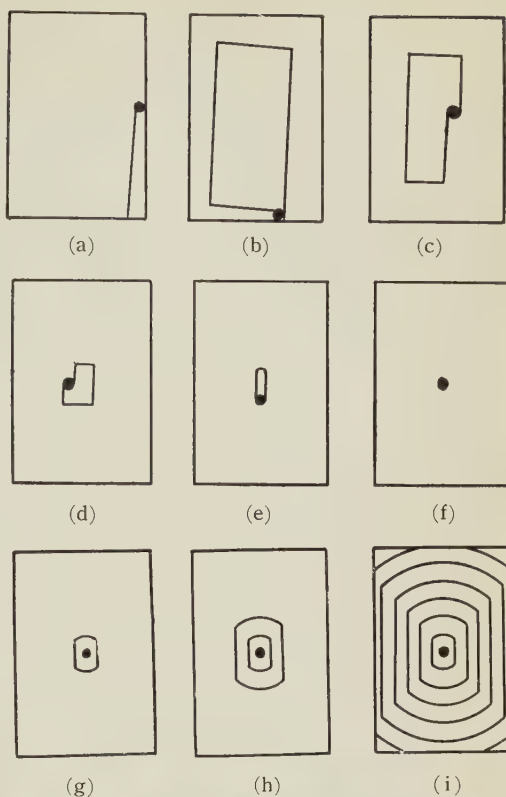


Photo. 2. Schematic illustration of the formation of closed loop step by a droplet, and its photograph.

motions, as fast as 200 times per minute, perhaps due to an inhomogeneous tension between solid and liquid. In these cases, however, it is not clear whether a very thin layer of molecular order was formed in the junction between two phases or not.

By a beautiful combination of the above-mentioned D.G. mechanism and ordinary layer formation, a building-up of closed loop steps was observed (Photo. 2).

Let a rectangle in the figure be a flat surface bounded by steps or borders in the crystal. Then a droplet which appeared at a corner travels along to a step or border (a) and turns successively at every corners (b)~(d), and is finally enclosed by its own new layer (e). After it is enclosed perfectly (f), it jumps up onto the new surface according to the crystallization in the part of a hole where the droplet has been enclosed, and simultaneously the ordinary layer formation starts around the droplet which acts as a nucleus for the formation of a closed loop steps (g). In a little while the droplet jumps up onto the closed loop step and forms the next loop step as before (h). And this process is repeated many times (i) forming a multiple loop step. The appearance of the closed loop steps is resemble to that formed by Frank's screw dislocation mechanism for crystal growth, but the higher step height is possible by this process, without being accompanied by a cluster of dislocations.

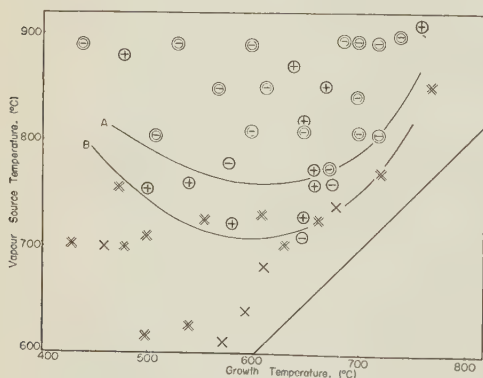


Fig. 2. Growth diagram. ⊙: Crystals were grown in case of slow cooling of MoO₃ vapour; ○: Crystals were grown in case of rapid cooling of MoO₃ vapour; ⊕: Droplets were recognized; -: Droplets were not recognized; ⊗: Crystals were not grown within 15 min in case of slow cooling; ×: Crystals were not grown within 15 min in case of rapid cooling.

A spiral growth may be also possible by another combination of the D.G. mechanism and ordinary layer growth. But it has not yet been observed so far.

§ 4. Experimental Results

In order to find out conditions for the origination of droplets, the growth diagram as shown in Fig. 2 was drawn for two kinds of the cooling speed. Curves A and B show the boundaries of crystal growth regions in the cases of slow and rapid coolings of the vapour respectively. It is characteristic that drop-

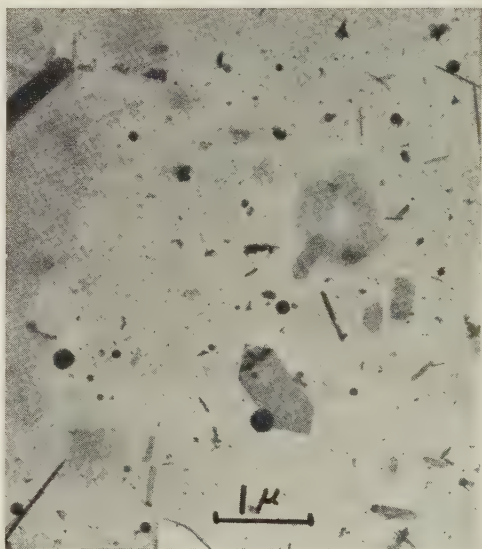


Photo. 3. Smoke of MoO₃ vapour cooled at moderate speed.

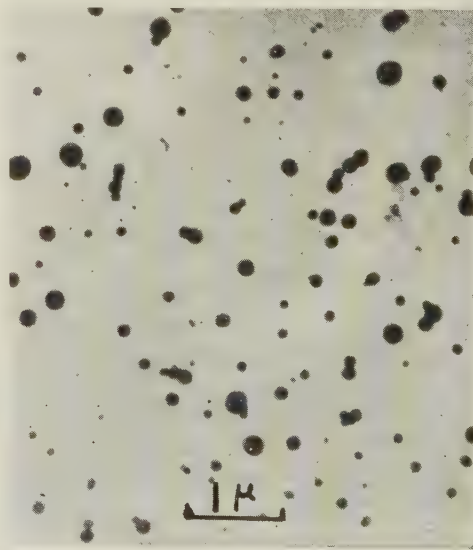


Photo. 4. Smoke of MoO₃ vapour cooled more rapidly than in the case of Photo 3.

lets were created when the vapour was cooled rapidly, but not slowly. Non-coincidence of the two curves *A* and *B* is partly due to the acceleration of crystal growth by D.G.

Photo. 3 shows smoke made by cooling the MoO_3 vapour which causes D.G. at the position of crystal growth, down to room temperature. There appear small spheres besides the MoO_3 crystals, and when the vapour was cooled more rapidly, the proportion of spheres increased, as shown in Photo 4. They were recognized even if the source temperature was held below the melting point of MoO_3 .

Table I. Observed spacings of MoO_3' (first row) and calculated values as a monoclinic: $a=4.550$ Å, $b=7.148$ Å, $c=9.113$ Å, $\beta=121.11^\circ$ (second row) and as a hexagonal: $a=8.996$ Å, $c=14.296$ Å (third row).

		Monoclinic		Hexagonal	
<i>d</i> (obs.)	<i>I</i> (obs.)	<i>d</i> (calc.)	(hkl)	<i>d</i> (calc.)	(hk·l)
3.89 ₅	V S	3.895	100	3.895	20·0
3.56 ₅	V S	3.574	020	3.574	00·4
3.42	S	3.420	110	3.420	20·2
2.70	W	2.713	111	2.685	10·5
2.63 ₅	S	2.635	022	2.635	20·4
2.31	VW	2.291	12 $\bar{3}$	2.305	20·5
2.14 ₅	M	2.138	112	2.145	22·2
2.03 ₅	W	2.034	130	2.034	22·3
1.93 ₉	VW	1.945	200	1.946	40·0
1.87 ₃	VW	1.871	22 $\bar{3}$	1.878	40·2
1.78 ₇	M	1.787	040	1.787	00·8
1.71 ₂	M	1.712	024	1.710	40·4
1.62 ₉	M	1.629	14 $\bar{2}$	1.624	20·8
1.55 ₀	VW	1.557	22 $\bar{5}$	1.550	50·1
1.49 ₄	M	1.495	30 $\bar{4}$	1.491	33·1
1.43 ₂	W	1.430	025	1.430	33·3
1.39 ₃	W	1.397	142	1.398	21·8
1.34 ₂	W	1.342	150	1.342	20·10
1.27 ₂	W	1.275	203	1.275	43·1
1.23 ₂	W	1.232	115	1.232	41·8
1.19 ₄	W	1.194	25 $\bar{1}$	1.193	42·7
1.14 ₂	W	1.142	036	1.140	60·6
1.09 ₇	W	1.093	251	1.097	61·5

Before solidification they had been in liquid state. By X-ray analysis of the powder corresponding to Photo. 3 and 4 it was found that there were two substances, MoO_3 and a new compound⁹⁾ with spacings tabulated in the first row of Table I.

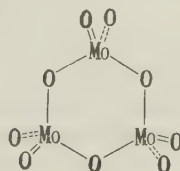
J. Berkowitz *et al.*⁷⁾ found the polymerization of the vapour phase and proposed a molecular model for Mo_3O_9^* which occupies the major part in gaseous species. If the vapour molecules were so constructed, the coordination number of oxygen around the Mo atom would be 4 and the O–Mo–O angle would be nearly equal to $2\pi/3$, whereas in MoO_3 crystal they are 6 and $\pi/2$ respectively. If it happens in the present case, the molecules in the crystallization from the vapour must suffer some rearrangement and some special circumstance can be expected.

By determining lattice parameters by Ito's method⁸⁾ it was analysed that the new compound belongs to monoclinic system: $a=4.550$ Å, $b=7.148$ Å, $c=9.113$ Å, $\beta=121.11^\circ$ (second row in Table I). But this system is very close to hexagonal system. Thus, recalculations were carried out arranging the parameters as a hexagonal system, obtaining $a=8.996$ Å, $c=14.296$ Å (third row in Table I). In the present stage, it is impossible to decide which of these two is correct, since a single crystal has not yet been prepared.

The new compound changed into MoO_3 perfectly at 500°C within 5 minutes in vacuum of 10^{-4} mm Hg, and since it is known that this atmosphere acts reductive on the molybdenum oxides⁹⁾ and that there is no higher oxide than MoO_3 , this new compound is stoichiometrically the same as MoO_3 , or metastable phase of MoO_3 , which is named temporarily as MoO_3' .

From the experimental results mentioned above, it can be supposed that the droplet consists of two molecular species, one having the same type of bonding as that of normal liquid (MoO_3) and the other having another type of bonding (MoO_3'), which will be called respectively solid type and gas type mole-

* The annexed figure is the configuration for Mo_3O_9 proposed by J. Berkowitz, W. G. Inghram and W. A. Chupka. The double-bonded oxygen atoms are above and below the plane of the ring, and the Mo–Mo distance is nearly equal to that in the solid MoO_3 .



cules. The mixing occurs so as to lower the free energy of a droplet. The solid type molecules can crystallize in the lattice sites but the gas type molecules must transform to the solid type molecules before crystallization. When the vapour condenses onto the droplet surface (Fig. 3), gas type molecules are abundant near the surface and the state is in a lower melting point owing to the increase of mixing entropy, and since the transformation of gas type to solid type molecules occurs in the interior, the crystallization occurs in the solid-liquid interface and thus the dynamic balance is maintained with the vapour supplied. The droplets originate from thermal and density fluctuation of adsorbed molecules, and are metastable. An interpretation of the constancy of the droplet size in D.G. will be given in Appendix.

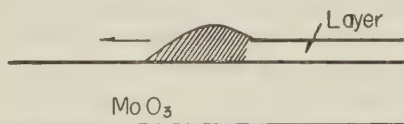


Fig. 3. The profile of D.G.

Moreover, the X-ray data obtained by microbeam method supported this conclusion, that is, the pattern showing the spacings characteristic to MoO_3' , MoO_3 and some others were obtained.

§ 5. Discussions

I. Examination of other possible causes of D.G.

As to the reason why, in the case of crystal growth from the vapour phase in general, the vapour passes through a liquid state before crystallization, several causes can be supposed. The possibility of these causes will be briefly examined on the basis of our observed results.

As a droplet freezes and melts at fairly low temperature below the melting point, there should be some reason of the lowering of the melting point in the droplet itself. Following few causes were examined.

a) *Impurity*: The lowering by an impurity was calculated to be $40\sim 45^\circ\text{C}$ for $X=1$ per cent, where X is the specific molar concentration of the solute. But in the sample used in the present experiment X was far smaller. The inclusion of an impurity cannot explain

the lowering of over 200°C , if any (see Fig. 2).

b) *Size effect*: When the crystal size is very small, the lowering of premelting temperature can be expected¹⁰⁾. The lowering is an order of 1°C for the radius of 1μ . Thus the size effect is entirely negligible.

c) *Lower oxides*: At high temperature, in low pressure of oxygen, MoO_3 is apt to be reduced to lower oxides by a little chemical or physical stimulation^{1), 4), 9)}. If these lower oxides are mixed with MoO_3 , the large lowering of the melting point may be expected. In the present experiment, special cares were taken to avoid inclusion of any impurity and the reduction of the sample. The silica boat and the furnace were preheated at 850°C for 3 hours, and the sample was recrystallized three times, and clean oxygen gas was passed through.

Although inert gas, argon, of 1 atmosphere, including hydrogen of 10^{-2} , 2×10^{-1} and 2 mm Hg was used, any increase in the number of droplets was not observed, though the morphological shape of crystals was much influenced.

II. Remark on the origination of droplets

The stability of liquid curvature is determined by the supersaturation ratio. Let r_c be the minimum critical radius of liquid sphere, with which vapour with the supersaturation ratio α can be in equilibrium state at a temperature T . Then droplets with larger diameters than r_c grow, whereas those with smaller diameters evaporate out. The relation between r_c and α is given by

$$\ln \alpha = \frac{2\sigma_L V_L}{RT r_c}, \quad (1)$$

where V_L is the liquid volume per mole. This formula gives $\alpha \approx 1$ for $r_c = 0.1\mu$. In the present experiment, the minimum value of α is about 5, so that the minimum critical radius is far smaller than the radii of the droplets. Thus the stability condition for the formula (1) is safely satisfied.

III. Closed loop steps

The closed loop steps shown in Photo 2 were formed in considerably high supersaturation. It is impossible to predict whether they can be formed or not in a low supersaturation. But, when the dislocation mechanism is not concerned in a step formation as the

present case, a step height is not restricted by the dislocation energy, and we can expect, even in a low supersaturation, a step with considerable height according to the situation.

Part II

§ 6. Acceleration of Growth of Layers and Needle Crystals

It was mentioned in the previous section that the speed of layer formation by D.G. was 1.5~10 times as large as the speed of ordinary layer formation, but under usual growth condition it was observed most frequently that the former was about 6 times as large as the latter. It is assumed that all the molecules within distances (i.e. the so-called mean displacements) λ_i ($i=a$ and c) along the a and c directions of adsorbed molecules contribute to the layer growth, and that molecules impinged directly upon the droplet with spherical surface of radius r make also contribution to the layer growth (Fig. 4). Under usual condition the supersaturation ratio is of order of $10\sim 10^3$, so that the evaporation from both the solid and liquid parts can be safely neglected from view-point of mass supply.

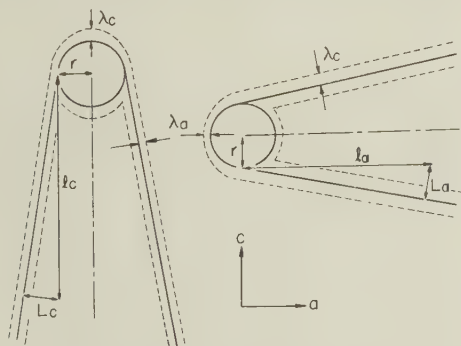


Fig. 4. Acceleration of layer formation by D.G. l_c/L_c and l_a/L_a are the acceleration ratios, while λ_c and λ_a are mean displacements along c and a directions of adsorbed molecules respectively.

If, in the ordinary layer growth, we assume that $\lambda_i < r$ as inferred from the growth velocity and the vapour pressure, the mass rate of impingement, W_i , of vapour molecules to the step side per unit length and per unit time is given by the formula:

$$W_i = (2\lambda_i + h)P \left(\frac{m}{2\pi kT} \right)^{1/2}, \quad (2)$$

where h is the step height, P the vapour pressure in the vicinity of the crystal and m the mass of the vapour molecule. Since, however, W_i is also equal to the mass increment of the layer, we can write

$$W_i = h\rho_s L_j \quad (j=c \text{ and } a) \quad (3)$$

where L_j is the speed of ordinary layer formation. Thus, from these two equations we get

$$L_i = \left(\frac{2\lambda_j + h}{h} \right) \frac{P}{\rho_s} \left(\frac{m}{2\pi kT} \right)^{1/2}. \quad (4)$$

On the other hand, the mass rate in D.G. w_i can be written as:

$$w_i = [\theta_i \pi r^2 + f_i \{ \pi (r + \lambda_a)(r + \lambda_c) - \pi r^2 \}] \times P \left(\frac{m}{2\pi kT} \right)^{1/2}, \quad 1 < \theta_i < 2 \quad (5)$$

where the first term in the square brackets is the contribution from the spherical surface which is an intermediate shape between a hemisphere and a circular disc, while the second term is that from the surface migration, which is approximated by the area enclosed between an ellipse with major- and minor-radii $(r + \lambda_a)$, $(r + \lambda_c)$ along a and c directions and a circle of radius r . f_i is a correction factor for overlapped portion in this approximation. We can assure that the mass ratio of crystallization is equal to w_i , because a volume of the droplet is invariable in D.G. process. As in the case of W_i , we may also write

$$w_i = 2rh\rho_s l_i, \quad (6)$$

where l_i is the speed of layer formation by D.G. to be expected from the mass rate w_i in Eq. (5). Solving (5) and (6) we have

$$l_i = \frac{\pi}{2} \frac{\theta_i r^2 + f_i \{ (\lambda_a + \lambda_c)r + \lambda_i \lambda_c \}}{r h \rho_s} P \left(\frac{m}{2\pi kT} \right)^{1/2}. \quad (7)$$

Thus, combining (4) and (7) we obtain the acceleration ratios as:

$$\left. \begin{aligned} \frac{l_c}{L_c} &= \frac{\pi}{2} \frac{\theta_c r^2 + f_c \{ (\lambda_a + \lambda_c)r + \lambda_c \lambda_c \}}{r (2\lambda_c + h)}, \\ \frac{l_a}{L_a} &= \frac{\pi}{2} \frac{\theta_a r^2 + f_a \{ (\lambda_a + \lambda_c)r + \lambda_a \lambda_c \}}{r (2\lambda_a + h)}, \end{aligned} \right\} \quad (8)$$

These ratios are independent of the vapour pressure, and the temperature is contained in λ_i implicitly and has only small effect, in accordance with the results of observation.

The values of these acceleration ratios can

Table II. Observed and calculated values of various quantities.

Suffix	l/L	r (in μ)	h (in μ)	θ	f	λ (in μ) (calc.)	λ_o/λ_o (calc.)	l_o/l_o (calc.)	L_o/L_o (calc.)	L_o/L_o (obs.)
c	7.75	1.0	0.1 ± 0.02	1.2	0.92	0.144	1.52	1.01	1.34	1.40
a	5.76	1.0	0.1 ± 0.02	1.2	0.88	0.095				

be obtained from Photo. 1 (a)* by measuring the angles of echelon type steps. θ_i and h can be measured by an interference microscope, and r is independent of the direction of movement, as confirmed by microscope and cinefilms in many cases. Also, f_i 's were estimated geometrically and determined self-consistently. Thus, using the values of these quantities, the values of λ_a , λ_c , l_c/l_a and L_c/L_a can be calculated from (4), (7) and (8). The results are tabulated in Table II, where are also given observed numerical values of various quantities at growth temperature 700°C.

As will be seen from the table, the mean displacement along the c -axis is larger than that along the a -axis, in accordance with the major growth direction. The speed of D.G. does not vary with the directions, which coincides with observations. The observed value of L_c/L_a is the mean of the ratio of major to minor radii in the loop steps in Photo 2, which was grown up at the almost same temperature as that in Photo. 1 (a). The slight discrepancy between the observed and calculated values of L_c/L_a may be due to the difference in the step heights.

Appendix

The constancy of the volume and the stability against the density fluctuation of the vapour supplied in D.G. process can be explained as follows.

The volume V and the surface area S of a droplet are given respectively by

$$V=V_s+V_g=\frac{\pi}{3}\frac{(2-\cos\varphi-\cos^2\varphi)}{(1+\cos\varphi)\sin\varphi}r^3,$$

$$S=\frac{2\pi}{1+\cos\varphi}r^2,$$

where V_s and V_g are the volume occupied by the solid and gas type molecules respec-

* It could be assured that there was no accidental change of growth condition before and after the turning of droplet, because the other parts of the crystal did not show any heterogeneity.

tively, φ and r are the contact angle and the radius of the liquid part respectively. Thus, the time-dependence of V_g can be represented by the formula:

$$\frac{dV_g}{dt}=\frac{pv_g}{\sqrt{2\pi mkT}}S+\frac{2\pi\lambda pv_g}{\sqrt{2\pi mkT}}r-\varepsilon V_g,$$

$\varepsilon>0 \quad (a)$

where v_g is the molecular volume. On the right-hand side of this equation the first term represents the supply of gas type molecules from vapour phase onto the droplet surface and the second term gives the supply of similar molecules by surface migration, while the last term gives the volume of the gas type molecules transformed to solid type ones. λ has the meaning of averaged mean displacement which is insensitive to the change of growth conditions and ε is a certain positive constant.

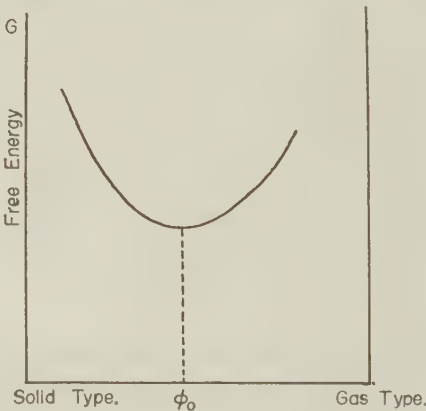


Fig. 1'.

The mixing rate should not differ so much from the minimum value ϕ_0 (Fig. 1'). Hence, we may write

$$V_g/(V_s+V_g)=\phi_0. \quad (b)$$

From (a) and (b) we get

$$\left|r-\frac{\alpha}{2}-\sqrt{\beta+\frac{\alpha^2}{4}}\right|^{1+\alpha/\sqrt{4\beta+\alpha^2}}\cdot\left(r-\frac{\alpha}{2}+\sqrt{\beta+\frac{\alpha^2}{4}}\right)^{1-\alpha/\sqrt{4\beta+\alpha^2}}$$

$$= C \exp\left(-\frac{2}{3} \varepsilon t\right), \quad (\text{c})$$

where

$$\alpha = \frac{6 \sin \varphi}{\varepsilon \phi_0 (2 - \cos \varphi - \cos^2 \varphi)} \cdot \frac{p v_g}{\sqrt{2 \pi m k T}},$$

$$\beta = \frac{6 \lambda \sin \varphi (1 + \cos \varphi)}{\varepsilon \phi_0 (2 - \cos \varphi - \cos^2 \varphi)} \cdot \frac{p v_g}{\sqrt{2 \pi m k T}}.$$

C being a constant of integration.

Eq. (c) shows that the radius of a droplet always converges to a finite value r_∞ as time increases and it is stable against the density fluctuation of vapour pressure which is contained in the factors α and β , that is,

$$\lim_{t \rightarrow \infty} r = \left\langle \frac{\alpha}{2} + \sqrt{\beta + \frac{\alpha^2}{4}} \right\rangle_{\text{av}} \equiv r_\infty,$$

$\langle \rangle_{\text{av}}$ denoting the time-average.

It should be pointed out that we can also get the same result by treating a differential equation for determining V_s instead of the differential equation (a) for V_g .

Acknowledgements

The author wishes to express his sincere gratitude to Professor K. Tanaka for his profound interest in the present work and for his valuable advice. The author's thanks are also due to Dr. H. Hashimoto, Dr. H.

Kiho, Messrs. S. Maruyama, T. Seto and Y. Fujiwara for their stimulating discussions and useful suggestions throughout this work.

References

- 1) H. Hashimoto: J. Phys. Soc. Japan **9** (1954) 150. T. Takagi: J. Mechanical Laboratory **6** (1952) 139. R. Ueda: Densikenbikyō **3** (1954) 43 (in Japanese).
- 2) König: Z. Phys. **130** (1951) 483; Optik **7** (1950) 261. H. Hibi and K. Yada: J. Electron-microscope, Japan **2** (1954) 45. O. Rang und F. Schleich: Z. Phys. **136** (1954) 547.
- 3) E. Yoda and H. Hashimoto: Metal Physics **4** (1958) 73 (in Japanese).
- 4) A. Magneli, G. Anderson, B. Blomberg and L. Kihlberg: Anal. Chem. **24** (1953) 1998.
- 5) S. Tanisaki: J. Phys. Soc. Japan **11** (1956) 620.
- 6) R. W. C. Wyckoff: *Crystal Structures* (Intersci. Publ.).
- 7) J. Berkowitz, M. G. Inghram, W. A. Chupka: J. Chem. Phys. **26** (1957) 842.
- 8) T. Ito: *X-ray Studies on Polymorphism* (Maruzen Co., Tokyo, 1950).
- 9) D. H. Killeffer and A. Linz: *Molybdenum Compounds* (Intersci. Publ., 1952). L. Kihlberg and A. Magneli: Acta Chem. Scand. **9** (1955) 471.
- 10) A. Skapski: Acta Metal. **4** (1956) 583.

The Change in Electron Mobility in Indium Antimonide at Low Electric Field

By Yasuo KANAI

Electrical Communication Laboratory, Musashinoshi, Tokyo

(Received December 14, 1959)

The change in electron mobility in indium antimonide at low electric field is measured by the bridge method at 77, 201 and 297°K. At 77°K the electron mobility decreases with increasing electric field in rather pure indium antimonide, but increases in impure one. At 201 and 298°K the change in electron mobility is too small to be detected. The effect of transverse magnetic field upon the change in electron mobility is also measured. In a transverse magnetic field, the electron mobility in indium antimonide increases with increasing electric field at 77°K, while it decreases at 201°K. At 297°K, the change in electron mobility in a transverse magnetic field is also too small to be measured.

To explain the experimental results mentioned above, some considerations are made on the scattering mechanism of conduction electron in indium antimonide. Then it is concluded that polar scattering is the most important in indium antimonide in the temperature range from 77°K to about 300°K, and also that the impurity scattering plays an important role in our samples at 77°K and acoustic scattering does some contributions at 201°K.

§ 1. Introduction

When an electric field is applied to a conductor, the distribution function for the conducting carrier deviates from the value corresponding to the thermal equilibrium state. In a high electric field the deviation will be fairly large, and the conducting carrier is called to be "hot", and the Ohm's law ceases to be valid because the mobility of conducting carrier varies with electric field. Even in a weak electric field, the deviation from the thermal equilibrium state occurs, so a small change in the mobility of conducting carrier also occurs.

The change in electron mobility in germanium at low electric field has been measured by a few investigators, and their results are referred in Gunn's report¹⁾. His report also contains the theoretical consideration upon the change in electron mobility with electric field. In the case of germanium, however, the experimental data do not agree with the theoretical value based upon simple assumptions. Recently Yamashita²⁾ calculated the change in electron mobility in germanium at low electric field, and he showed that, if the optical scattering, as well as acoustic scattering, is taken into account, the agreement between the experimental data and the theo-

retical value is fairly good.

As is well known, the electron mobility in indium antimonide is quite large. Hence it may be expected that the change in electron mobility in this material will be measurable at low electric field. In this paper some experimental results on the change in electron mobility in indium antimonide are reported, and then, to explain the experimental data, some considerations are made upon the scattering mechanism of conduction electron.

§ 2. Experimental Procedures

2.1 Measuring apparatus

To measure the small change in electron mobility in indium antimonide at low electric field, we used the bridge method as Gunn¹⁾ did already in the measurement on germanium. Fig. 1 shows the schematic representation of the measuring circuit. To avoid the heating

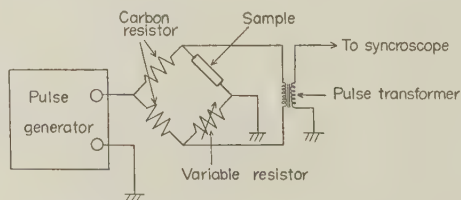


Fig. 1. Schematic representation of measuring circuit.

effect, pulsed electric field of the width of 2 μ sec and the repetition rate of about several ten per sec was applied to the bridge circuit. As the variable resistor shown in Fig. 1, a dial resistor usable up to 5 Mc/s and 0.1 ohm stop was used. As the null indicator a syn-croscope was used. By these arrangements the relative change in the resistivity of sample was measured within the accuracy of 0.1 per cent.

At low electric field, the number of conduction electron will not vary with applied field, so the change in resistivity of the sample may be attributed to the change in electron mobility. Therefore the following relation is valid at low electric field; $\rho/\rho_0=\mu_0/\mu$, where

the subscript 0 means the value at vanishingly small electric field. By this relation the change in electron mobility in electric field was determined from the resistivity change which was measured by the bridge circuit shown in Fig. 1.

2.2 Preparation of the samples

All of the samples used in this experiment were cut from the same crystals which were used already in the experiment of breakdown at high electric field, and the details of the method of preparing the samples were described in that report³⁾. In Table I some electrical properties of our samples used in this experiment are summarized.

Table I. Some electrical properties of our samples.

Sample No.	Degenerate temperature in °K	Uniformity in per cent	Resistivity (ρ) in ohm-cm	Hall coefficient (R) in cm ³ /coul.	Hall mobility (μ_H) in cm ² /V.sec	Electron density (n) in no./c.c.
1	17.5	12	77°K 7.55 $\times 10^{-2}$	-1.58 $\times 10^4$	2.09 $\times 10^5$	3.95 $\times 10^{14}$
			201°K 4.1 $\times 10^{-2}$	-5.8 $\times 10^3$	1.4 $\times 10^5$	1.1 $\times 10^{15}$
3	37	8.3	77°K 2.32 $\times 10^{-2}$	-5.05 $\times 10^3$	2.18 $\times 10^5$	1.23 $\times 10^{15}$
			201°K 2.9 $\times 10^{-2}$	-3.2 $\times 10^3$	1.1 $\times 10^5$	2.0 $\times 10^{15}$
5	74	5.7	77°K 1.95 $\times 10^{-2}$	-1.80 $\times 10^3$	9.22 $\times 10^4$	3.46 $\times 10^{15}$
			201°K 1.88 $\times 10^{-2}$	-1.63 $\times 10^3$	8.68 $\times 10^4$	3.82 $\times 10^{15}$

§ 3. Experimental Results

3.1 The change in electron mobility at various temperatures

The changes in electron mobility in indium antimonide at low electric field were measured at 77, 201 and 297°K. The experimental results at 77°K are shown in Fig. 2. In this figure we can see that the change in electron mobility at low electric field may be expressed by the following relation; $\mu=\mu_0(1+\beta E^2)$. The values of β for our samples are also shown in Fig. 2. At 201 and 297°K, the change in electron mobility of our samples was also measured, but it was too small to be detected; i. e. $\beta \simeq 0$.

3.2 The change in electron mobility in a transverse magnetic field

The change in electron mobility at low electric field was also measured in a transverse magnetic field at 77, 201 and 297°K. The results obtained at 77°K and in a transverse magnetic field of 660 gauss are shown in Fig. 3. From Figs. 2 and 3, we may find that the value of β varies when a transverse

magnetic field is applied. In Fig. 4 the values of β for our samples at 77°K are shown as

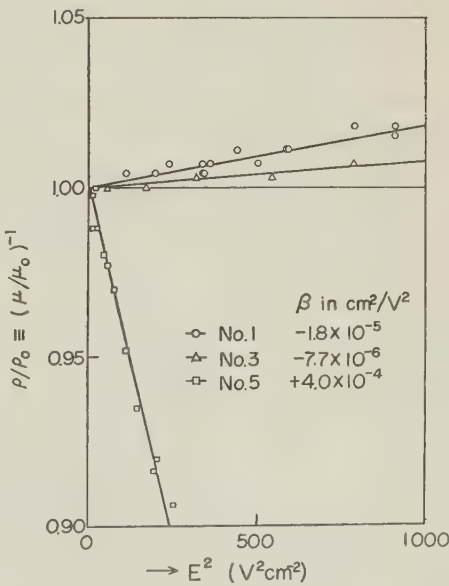


Fig. 2. The change in electron mobility in indium antimonide at 77°K.

functions of the magnetic field strength. In this figure we can see that, when the magnetic

field increases the values of β for all samples become positive and reach some saturation values. In Fig. 5, the values of β for our samples at 201°K are shown as functions of the magnetic field strength. As is shown in this figure, the values of β have the negative sign at this temperature, and the absolute values of β increase with increasing magnetic field strength. At 297°K the values of β were too small to be detected even in a magnetic field strength of about 6 kilo gauss.

§ 4. Discussion

As has already been discussed in Gunn's report¹⁾, the value of β depend on the scattering mechanism of conduction electrons. So, to explain our experimental results, it is necessary to know what scattering mechanism is dominant in indium antimonide. A few years ago, Ehrenreich⁴⁾ calculated the temperature dependence of electron mobility in indium antimonide in the temperature range from 200°K to 700°K, and he found that lattice scattering by polar mode with $e^*=0.18e$

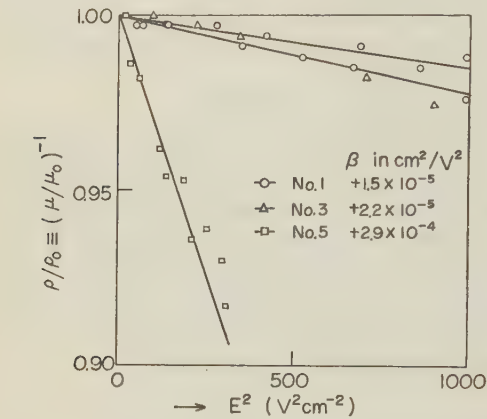


Fig. 3. The change in electron mobility in indium antimonide at 77°K and in a transverse magnetic field of 660 gauss.

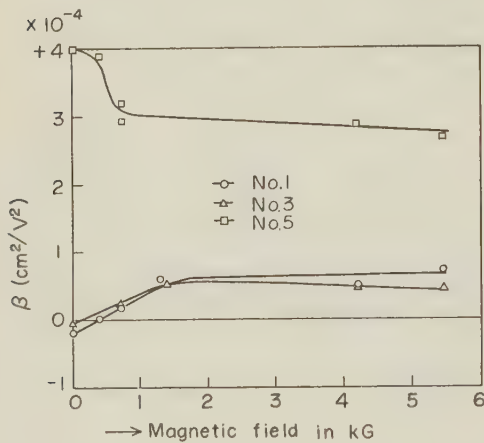


Fig. 4. The values of β as functions of the transverse magnetic field at 77°K.

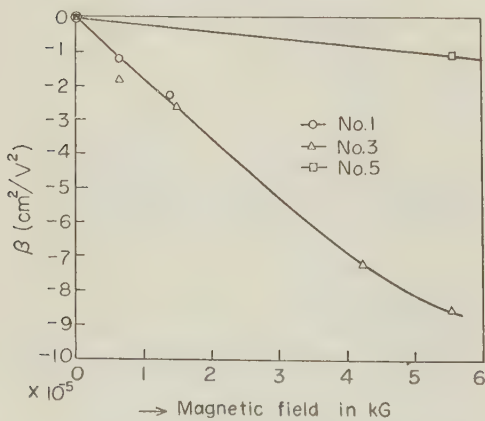


Fig. 5. The values of β as functions of the transverse magnetic field at 201°K.

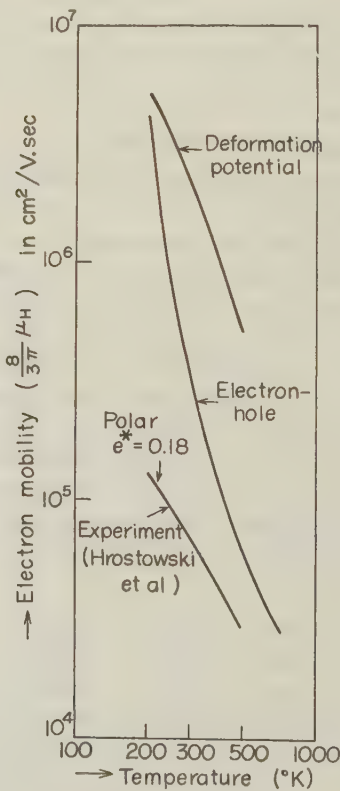


Fig. 6. Electron mobility versus temperature curves for various scattering mechanism in indium antimonide. (After Ehrenreich)

could explain the experimental data quite well, which was taken from the work done by Hrostowski et al⁵⁾. In Fig. 6 Ehrenreich's theoretical result is shown, and in Fig. 7 the electron mobility of the samples of Hrostowski et al and of ours are both shown. In Fig. 7 we can see that, below about 200°K the electron mobility of our samples differs from that of the sample of Hrostowski et al because of the low purity of our samples, but above 200°K the agreement between our data and that of Hrostowski et al is good.

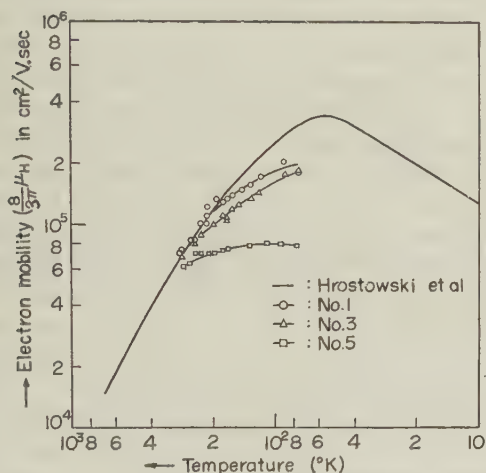


Fig. 7. Electron mobility *versus* temperature curves for various samples of indium antimonide.

Now we shall begin our discussions by explaining the experimental values of β which have been measured at 77°K and without magnetic field. As we can see in Fig. 2, the values of β for samples No. 1 and 3 have negative sign but that for sample No. 5 has positive sign; i. e., the value of β for impure sample is positive. As the value of β for a sample in which impurity scattering is predominant has positive sign, the experimental results mentioned above are quite reasonable. Then let us consider our results more quantitatively. If the lattice scattering of acoustic mode is primarily important in indium antimonide at 77°K, then the value of β for a pure sample will be expressed by the following relation¹⁾; $\beta = -3\mu_{L0}^2/16c^2$ where μ_{L0} is the electron mobility in a pure sample at vanishingly small electric field, and c is the sound velocity. As is well known, μ_{L0} must be very large in indium antimonide, so β will become

also quite large (probably $0.1-1 \text{ cm}^2/\text{V}^2$). In an impure sample the absolute value of β will decrease because of the coexistence of the impurity scattering. Gunn's calculation shows, however, that the order of magnitude of the value of β in an impure sample does not differ greatly from the value of β corresponding to the pure one. As are shown in Fig. 2, the experimental values of β for our samples is of the order of $10^{-4}-10^{-5} \text{ cm}^2/\text{V}^2$, hence we may conclude that lattice scattering of acoustic mode is not predominant in indium antimonide at 77°K.

Then we shall consider that the lattice scattering of optical mode is predominant in indium antimonide at 77°K. Recently Stratton⁶⁾ calculated the value of β and the breakdown voltage for a polar semiconductor, and he applied his results to indium antimonide. His results are summarized as follows; If the electron density in indium antimonide exceeds the value 1×10^{13} (at 100°K) or 3×10^{13} (at 200°K), the interelectronic collision would play an important role in the determination of distribution function, and then β for a pure indium antimonide at lattice temperature T_0 would have the value as shown in Fig. 8.

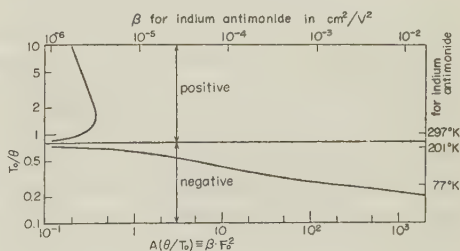


Fig. 8. The value of β *versus* lattice temperature T_0 curve for a polar semiconductor when the interelectronic collision predominates (After Stratton). For indium antimonide $\theta=290^\circ\text{K}$ and $F_0=340 \text{ V/cm}$.

In this theoretical curve we can find that the value of β for a pure indium antimonide at 77°K will become about $-1 \times 10^{-3} \text{ cm}^2/\text{V}^2$. As there is no calculation for the semiconductor in which both polar scattering and impurity scattering coexist, we can not determine exactly what value β should have in impure indium antimonide. However, by analogy with the case for the semiconductor in which both the acoustic scattering and impurity scattering coexist, we may believe that the value of β for an impure indium antimonide

would be approximately the order of magnitude of $10^{-4} \text{ cm}^2/\text{V}^2$. As this order of magnitude is the same as that of the experimental data, it seems most likely that polar scattering is most predominant in indium antimonide at 77°K.

From Stratton's results shown in Fig. 8 we can find also that theoretical values of β for indium antimonide at 201 and 297°K are approximately -2×10^{-6} and $+2 \times 10^{-6} \text{ cm}^2/\text{V}^2$ respectively. These values are too small to be detected by our measuring apparatus, while the measured values of β at 201 and 297°K are approximately zero. Thus our experimental results on the change in electron mobility in indium antimonide at low electric field are consistent with Stratton's theoretical results. Hence we may conclude that, at least in the temperature range between 77°K and 297°K, the polar scattering is the most important scattering mechanism for conduction electron in indium antimonide.

Next, let us consider the effect of transverse magnetic field upon the value of β . As is written in Gunn's report, the value of β depends on the scattering mechanism of conduction electron in the sample. For instance, in impure semiconductors the value of β is determined by the mobility ratio μ_{L_0}/μ_{I_0} ($\equiv \alpha$), where μ_{L_0} is the low field mobility determined by lattice scattering only and μ_{I_0} is the low field mobility determined by impurity scattering only. As is shown in Figs. 4 and 5, the values of β in our samples depend on the strength of the transverse magnetic field, hence it may be reasonable to consider that the value of α depends on the magnetic field. To calculate the value of α in a transverse magnetic field, the mobility ratio is an inconvenient quantity; hence, instead of it, the resistivity ratio may be adopted as a useful representation for α in a magnetic field; i. e. $\alpha \equiv \mu_{L_0}/\mu_{I_0} = \rho_{I_0}/\rho_{L_0}$, where ρ_{I_0} is the low field resistivity determined by impurity scattering only, and ρ_{L_0} is the low field resistivity determined lattice scattering only. In a magnetic field ρ_{I_0} and ρ_{L_0} increase due to the magnetoresistance effect, but the increment in ρ_{I_0} is larger than that in ρ_{L_0} . Hence, α increases, i. e. the impurity scattering becomes predominant with increasing magnetic field, so the value of β tends to positive value in rather pure samples (No. 1 and 3), and in the impure

sample (No. 5) the value of β tends to the small value. Thus our experimental results shown in Fig. 4 are well explained by assuming that both impurity scattering and lattice scattering coexist in our sample at 77°K.

At 201°K impurity scattering will become very weak and other scattering mechanism, for instance, electron-hole scattering will become important (See Fig. 6). In the case of electron-hole scattering, however, the energy dependence of collision time would be similar to the case of impurity scattering, so the value of β should become positive in a transverse magnetic field. This prediction contradicts to the experimental results shown in Fig. 5. Hence, to explain our experimental results of indium antimonide at 201°K, another scattering mechanism, i. e. acoustic mode scattering must be considered. In the case of the coexistence of polar scattering and acoustic scattering, α should be replaced by another form, i. e. $\alpha \equiv \rho_{a_0}/\rho_{p_0}$, where ρ_{a_0} is the low field resistivity determined by acoustic scattering only and ρ_{p_0} is the low field resistivity determined by polar scattering only. In a magnetic field the increment in ρ_{a_0} is larger than ρ_{p_0} , hence acoustic scattering become predominant and β becomes a larger negative value. This prediction is consistent with our experimental results which are shown in Fig. 5. Hence we may believe that the acoustic scattering, instead of electron-hole scattering, plays some role in indium antimonide at 201°K.

§ 5. Conclusion and Acknowledgement

The changes in electron mobility in indium antimonide were measured by bridge method at 77, 201 and 297°K, and it was found that the changes in electron mobility at low electric field are well expressed by the theoretical formula; $\mu = \mu_0(1 + \beta E^2)$. At 77°K the values of β were positive in an impure indium antimonide but negative in two purer samples. At 201 and 297°K the values of β were too small to be detected. It was found also that the values of β changed by applying a transverse magnetic field. In a transverse magnetic field, the values of β of all samples became positive at 77°K, but negative at 201°K, and there were no changes at 297°K.

To explain the experimental results men-

tioned above, some scattering mechanisms of electrons in indium antimonide were considered, and following conclusions were reached; (A) Lattice scattering by polar mode is most important in indium antimonide. (B) At 77°K impurity scattering coexists in our samples. (C) At 201°K acoustic scattering rather than electron-hole scattering is important.

The author wishes to express his thanks to Dr. T. Niimi for his kind guidances and to Messrs. R. Nii and N. Watanabe for their valuable helps.

References

- 1) J. B. Gunn: *Progress in Semiconductors* **2** (1957) 213.
- 2) J. Yamashita: *Phys. Rev.* **111** (1958) 1529.
- 3) Y. Kanai: *J. Phys. Soc. Japan* **14** (1959) 1302.
- 4) H. Ehrenreich: *J. Phys. Chem. Solids* **2** (1957) 131.
- 5) H. J. Hrostowski, F. J. Morin, T. H. Geballe and G. H. Wheatley: *Phys. Rev.* **100** (1955) 1672.
- 6) R. Stratton: *Proc. Roy. Soc. A*, **246** (1959) 406.
- 7) A. H. Wilson: *The Theory of Metals* (Cambridge Univ. Press, 1953)

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

Visible Light Emission and Microplasma Phenomena in Silicon $p-n$ Junction, I.

By Makoto KIKUCHI

Electrotechnical Laboratory, Tokyo, Japan

and Kenkichi TACHIKAWA

Research Laboratory, Meiden-sha, Shinagawa, Tokyo, Japan

(Received December 14, 1959)

Experimental results on the visible light emission and microplasma phenomena in silicon $p-n$ junction are described. It has been found that the microplasma spot in the $p-n$ junction can be located by scanning small chopped light spot on the junction surface. Combining this method of location of the microplasma spot and the observation by microscope, it is concluded that the light emitting spot does not necessarily coincide with the microplasma spot.

Possibility of the effect of impurities on the light-emitting phenomena is discussed briefly in connection with our recent experimental result on the visible light emission from germanium $p-n$ junction. A simple model of $p-n$ junction is proposed for the understanding of microplasma phenomenon.

§ 1. Introduction

It has already been observed that visible light is emitted from reverse-biased $p-n$ junction in silicon¹⁾, which has been attributed to the recombination and intra-band transition of energetic carriers in the space charge layer. Chynoweth, et al.²⁾ have found out that the pattern of the light-emitting small spots corresponds to that of dislocation etch pits.

It is also found that sharp current pulses

of constant height appear in reverse-biased silicon $p-n$ junction³⁾. The height, width, and repetition rate of the pulses are dependent on the bias voltage. The pulses disappear as the reverse bias voltage is increased, but the second pulse appears as the voltage is further increased. Since this phenomenon has been analyzed in analogy with the gas discharge, which is famous as the Townsend process, it has been named "microplasma". Rose⁴⁾ pointed out that it is natural to cor-

relate the light-emitting spots with the microplasma spots.

The points of interest and questions concerning these phenomena may be summarized as follows:

(1) The spectral intensity of the emitted light extends far beyond the wave length which corresponds to the energy gap of silicon⁵⁾.

(2) Visible light emission phenomena have not been reported on germanium p - n junction until recent report of the authors⁶⁾.

(3) Does the light-emitting spot really coincide with the microplasma spot?

(4) In what way are the avalanche and Zener effects playing significant role in these phenomena?

In our preliminary experiments, microplasma and visible light emission were observed on metal-silicon contact formed by applying Ag paste⁷⁾. Remarkable jump was found in reverse current-voltage characteristic where light-emitting spot appeared on the periphery of the Ag paste electrode. As will be mentioned in the later section, hysteresis effect was found in the case of metal-silicon contact. Therefore, with proper load resistance, triggering action could be performed by illumination.

Most part of this article is, however, devoted to the description of the experiments on the diffused silicon junction, since the measurements are far more reproducible for

the diffused junction than the Ag paste electrode.

Observation of the light emission phenomena, microplasma pulses, and location of the microplasma spot by chopped light spot, are mentioned, and brief discussion is given in the last section on the correlation between the microplasma and light emission.

§ 2. Experimental Procedures

2.1 Preparation of samples

Eagle-Picher silicon was pulled in $\langle 111 \rangle$ direction doped with antimony. The single crystal was then sliced in (111) plane about 1 mm in thickness. Diffusion of boron was then performed in the furnace as shown in Fig. 1. The thickness of the diffused p -type layer ranged from 1 to 1.5 microns, since thick layer would prevent the observation of light emitting spots in the junction. After each diffusion, thickness of the layer was checked by oblique-polishing and staining techniques.

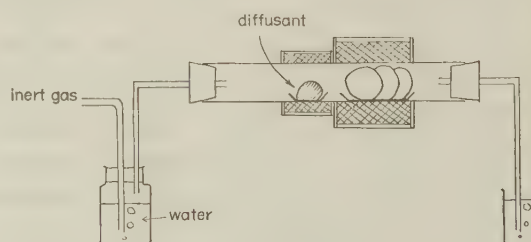


Fig. 1. Experimental apparatus used for performing diffusion.

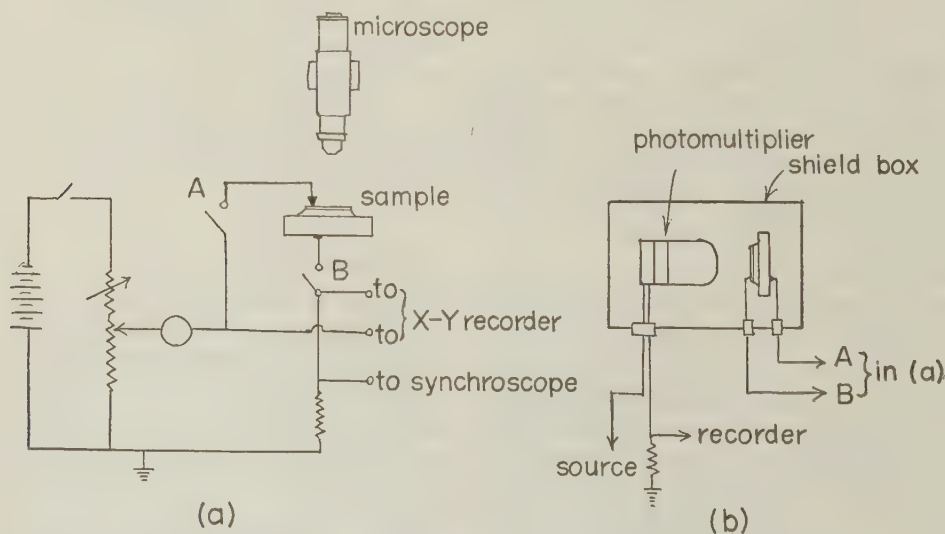
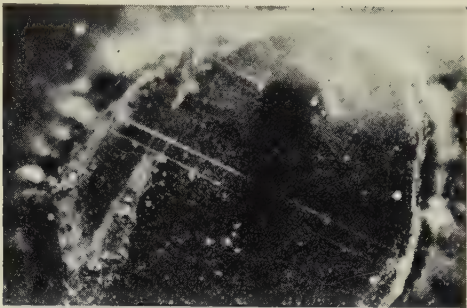


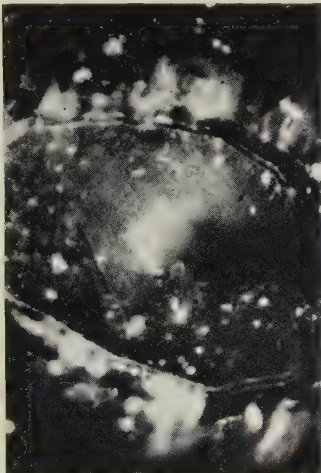
Fig. 2. Schematic representation of measuring circuits. (a) for measurements of current-voltage characteristic and microplasma pulses. (b) for measurement of light output.



Fig. 4. Photograph of light emitting spots in silicon diffused junction.



(a)



(a)



(b)

Fig. 5. Example of bright white spots in silicon junction. (a) is the photograph of the junction area, and (b) is the photograph of the light emitting spots.



(b)

Fig. 7. Light emitting spots corresponding to scratch on the surface.



Fig. 10. Light emitting spots appearing like the milky way.

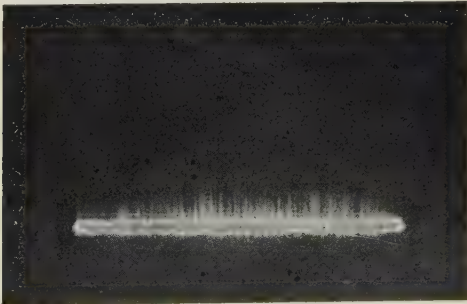


Fig. 11. Photograph of microplasma pulses observed on synchroscope.

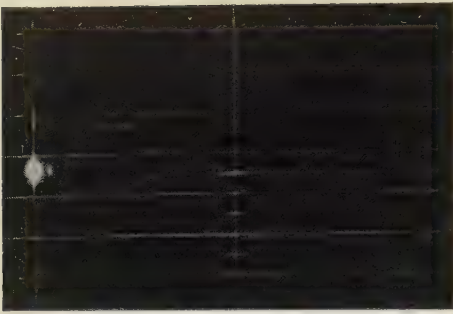


Fig. 12. Photograph of a microplasma pulse. (10 microsec/div.)

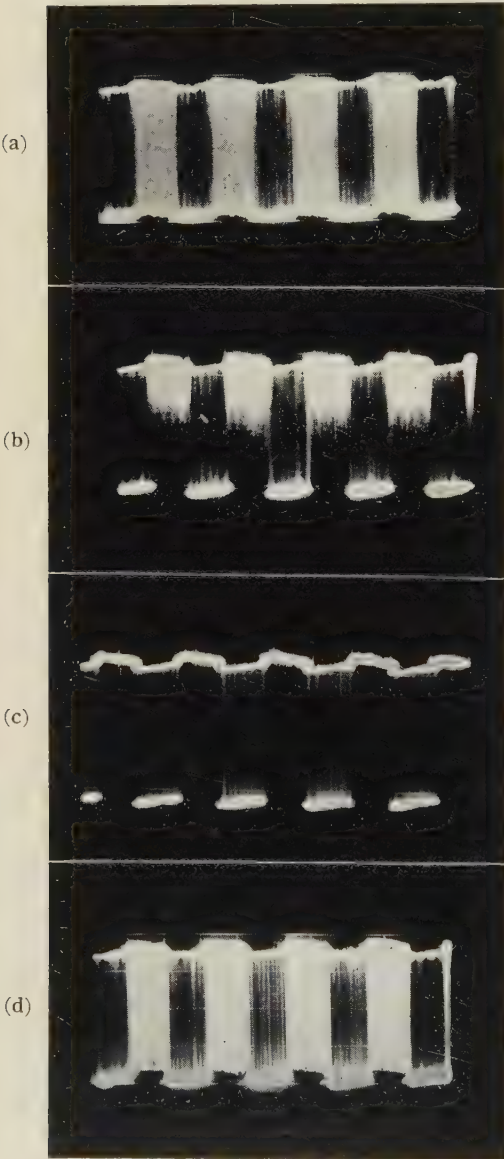


Fig. 18. Patterns observed on synchroscope when chopped light spot is scanned on the junction plane.

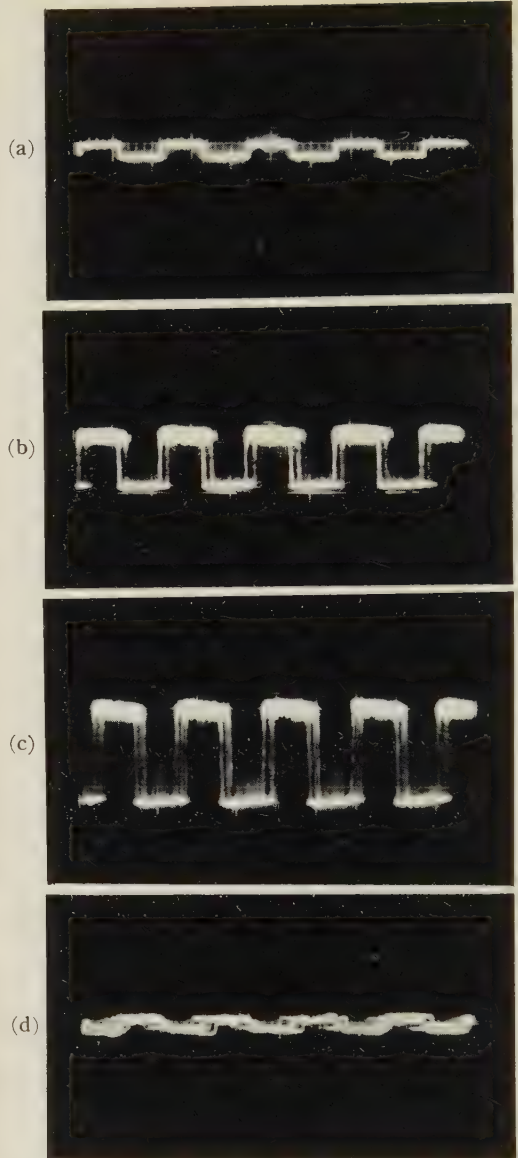


Fig. 26. Apparent carrier multiplication with microplasma pulses.

Small area, about 1–2 mm in diameter, was protected by wax and the sample was then subjected to etching.

2.2 Measuring apparatus

The sample is mounted on a micromanipulator and metal point contact is pressed on the *p*-type layer. Light emitting spots are observed by microscope, and current-voltage characteristic is traced on *x*–*y* recorder as shown in Fig. 2(a). Microplasma pulses are observed on Iwasaki No. 5301 synchroscope. Measurement of the light output is performed as shown in Fig. 2(b) using Toshiba No. 7306

photomultiplier tube and high sensitivity recorder. Since remarkable creeping is found in the current and light output in the case of Ag paste electrode, the recorder is specially designed to have small time constant.

In Fig. 3, experimental arrangement for the observation of the carrier multiplication and for the location of microplasma spots is shown schematically.

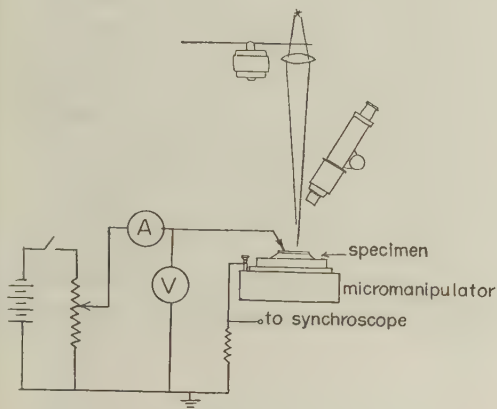


Fig. 3. Experimental arrangement for observing carrier multiplication and also for locating the microplasma spots.

§ 3. Experimental Results

3.1 Observation of the light emitting spots

Light emitting spots appear as the reverse bias voltage is increased. Typical example is shown in Fig. 4. Though the color is not shown in the figure, white or yellowish white spots appear on the periphery of the junction, while yellow or reddy spots are observed in the junction area through the diffused p -type layer. This may be attributed to the absorption of light of shorter wave length by the silicon layer above the junction. It must be noted here, however, that in some cases very bright white spots can be observed in the junction area as shown in Fig. 5(b). According to the viewpoint of light absorption mentioned above, these bright spots must be attributed to the fact that the light emitting spots are located quite near from the surface of the p -type layer. However, apparent imperfections which might cause misformation of the diffused layer (as shown in Fig. 6) could not be found on the surface by microscope.

In some cases, correlation between the light emitting spots and the flaw on the surface

could be clearly observed. Typical example is shown in Fig. 7. In this case, light emitting spots appear in a line (Fig. 7(b)), which correspond to a scratch caused by grinding before the diffusion (Fig. 7(a)) observed by microscope.

It is noticed that, in contradiction to the experimental results of Chynoweth, et al.²⁾, one-to-one correspondence between the dislocation etch pit and light emitting spot could not be necessarily found. The surface of the silicon wafer was etched³⁾ and dislocation etch pits were revealed at first. Diffusion was then performed on this surface and the small area $p-n$ junction was prepared by mask-etching. As is shown in Fig. 8, most of the light emitting spots appear on the flat surface and very few are found in the etch pits.

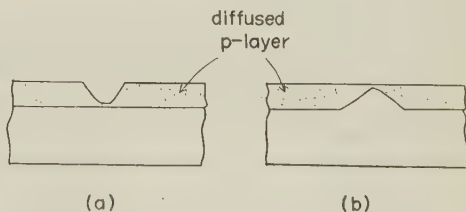


Fig. 6. Examples of misformation of diffused layer.

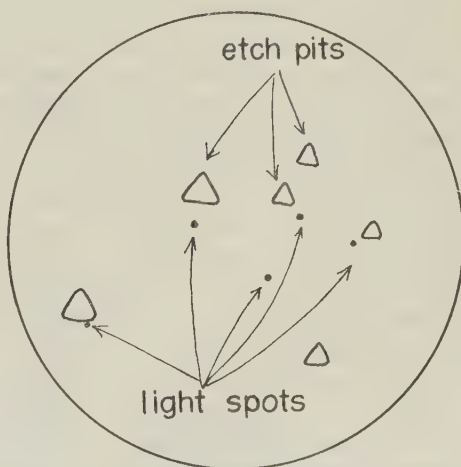


Fig. 8. Sketch of the observation of silicon surface by microscope.

A crystal containing boundary plane was cut into slices and the specimen was prepared as shown in Fig. 9. In this case, no special appearance of light emitting spots could be found along the grain boundary.

Fig. 10 shows an interesting result of the observation of the spots. As is seen in the photograph, small reddy spots appear like the milky-way in the sample. Two bands of spots are running nearly in parallel. The width of a band is approximately 50 microns.

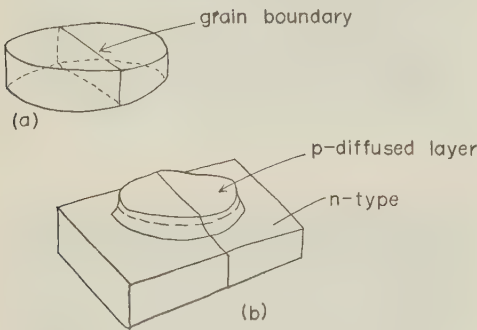


Fig. 9. Preparation of specimen from a crystal containing grain boundary.

In the specimen whose p -type layer is 0.75 micron in thickness, it has been observed that the small reddy spots appear only in the region of approximately 50 microns in diameter centered at the metal point contact on the p -type layer. This region migrated as the metal point was drawn on the surface. This phenomenon may be attributed to the lateral voltage drop in the p -type layer.

Temperature dependence of the light emitting properties of diffused p - n junctions was observed qualitatively. The temperature was lowered down to liquid oxygen temperature. The backward current-voltage characteristic and the appearance of light spots were scarcely modified by the temperature change. In the experiment performed in the room air, frost was formed on the surface as the sample was cooled and it was melted into water drops when the temperature was raised again. The light emitting spots could be observed in a similar pattern on the surface through the frost and water drops. The color of the spots was not changed in this treatment. These experimental results on the dependence of the light emitting properties of junction are consistent with the results of Chynoweth, et al.⁹⁾. The insensitive temperature dependence of the backward current is not so surprising since the backward current observed in this voltage range is not the simple saturation current but the "voltage dependent" current which may consist of recombination-generation

current, surface leakage current, and self-multiplicative current.

3.2 Microplasma pulses

When the reverse bias is increased to certain critical voltage, sharp current pulses of constant height and nearly constant width appear as shown in Fig. 11. The shape of

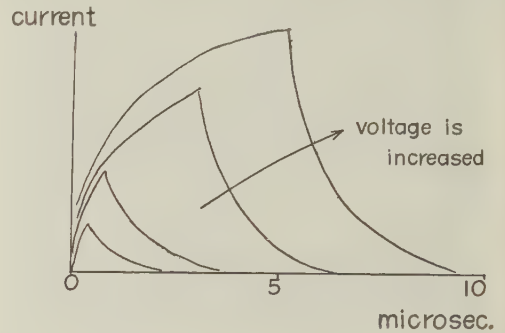


Fig. 13. Voltage dependence of the shape of pulse.

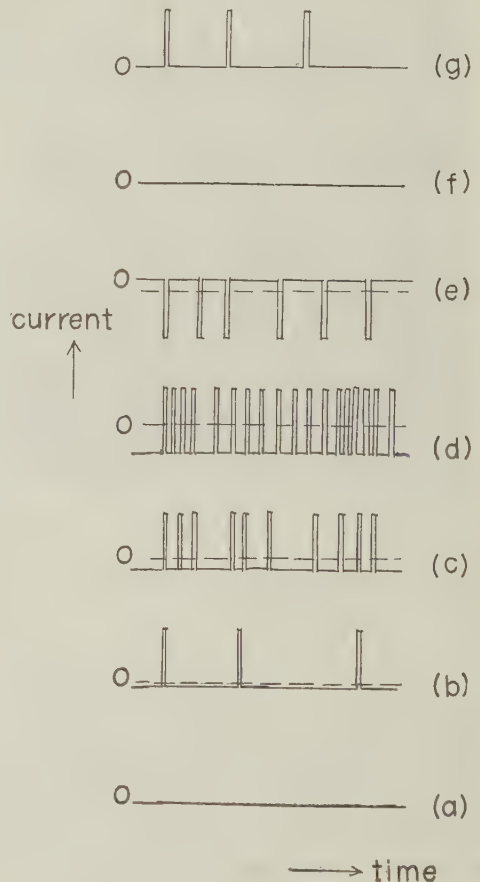


Fig. 14. Schematic representation of the appearance and disappearance of microplasma pulses according to the voltage variation.

a pulse in shown in Fig. 12, which depends on the condition of the measuring circuits. The height, width and repetition rate of the pulses are dependent on the bias voltage. Typical example is illustrated schematically in Fig. 13. Above three are all increased at first with increasing bias voltage, but the height is soon saturated and repetition rate is decreased. Schematic representation of this phenomenon is given in Fig. 14. As the voltage is increased ((a) to (g)), microplasma pulses appear ((b)), the repetition rate increases ((c), (d)), and finally, individual pulses can not be separated because of high repetition, which results in apparent negative current pulses ((e)). Microplasma pulses disappear for the bias voltage slightly above this condition. However, if the voltage is further increased, next plasma pulses appear at certain voltage ((g)) and the similar situations to (b)-(f) repeats again.

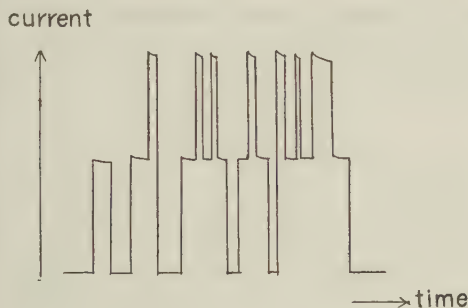


Fig. 15. Complex form microplasma pulses.

In some cases, microplasma pulses of the form shown in Fig. 15 are observed. In this case, the pulses are not the simple "ON"-"OFF" form, but they reveal two different "ON" states¹⁰⁾.

In general, pulse height ranges between 30 and 300 microamp., and the pulse width for lower voltage conditions ((b)-(d) in Fig. 14) ranges between 1 and 10 microsec.. It is noted here that, in the case of Ag-paste electrode experiment, pulse width is much higher, i.e., 50 to 500 microamp., and also that the pulse shows initial decay and fluctuation (noise).

3.3 Current-voltage characteristic and the microplasma pulses

As already mentioned previously¹¹⁾, strong hysteresis effect is observed in current-voltage characteristic of Ag-paste electrode on silicon

surface, corresponding to the occurrence of microplasma pulses and light emission. (Fig. 16(a)) As is shown in the figure, microplasma pulses appear near the voltage V_2 and the current jumps to high conduction state at V_2 . The current does not decrease to point A at V_2 for decreasing voltage, but it jumps to low conduction state at voltage V_1 . Light spot can be observed to appear on the periphery of the Ag paste electrode when the current jumps to high conduction state at voltage V_2 .

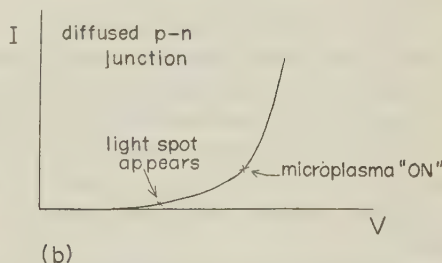
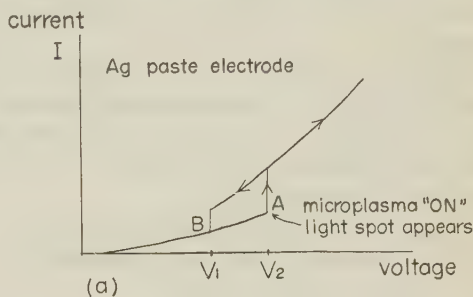


Fig. 16. Current-voltage characteristics of (a) Ag-paste electrode and (b) diffused $p-n$ junction.

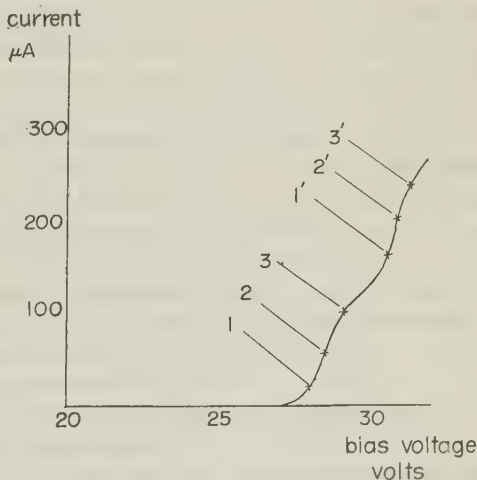


Fig. 17. Current-voltage characteristic and the occurrence of pulses.

In the case of diffused p - n junction reported here, however, the situation is quite different. As is shown in Fig. 16(b), current-voltage characteristic does not reveal hysteresis loop. Moreover, apparent coincidence between the light emission and microplasma pulses can not be clearly observed, which will be mentioned in 3.6 in more detail.

In general, it can be concluded that the microplasma pulses appear at voltages above the value where the current starts to grow up. Therefore, it may be natural to expect the correspondence between the "rising-up" current component and the microplasma phenomenon.

Successive occurrence and fading-out of pulses are shown in current-voltage characteristic in Fig. 17. The curve has been re-traced from x - y recorder. In the figure, 1, 2 and 3 show the situations,

- 1...positive pulses are observed,
- 2...negative pulses are observed,
- 3...pulses have faded out,

respectively.

3.4 Location of the microplasma spots

It has been found that the microplasma spots could be located in the junction by using the experimental arrangement shown in Fig. 2(a). A small light spot chopped at 225 cps is scanned on the junction surface by the micromanipulator on which the specimen is mounted.

Microplasma pulses appear when the reverse bias is increased up to certain voltage as shown in Fig. 11. When the chopped light spot comes in the vicinity of the microplasma spot, the pattern on the synchroscope becomes to that shown in Fig. 18(a). As is seen in the figure, not only the photocurrent appears in the "OFF" and "ON" states, but also the modulation occurs in the density of the microplasma pulses. As the chopped light spot comes nearer, probability of the state to stay at "ON" condition is increased in the illuminated period, and finally it becomes to unity as shown in Fig. 18(c). When the chopped light spot passes through the microplasma spot, the pattern becomes to that shown in (d). Watching the pattern on the synchroscope, therefore, one can determine the position of the microplasma spot on the surface of the specimen.

Mapping of the microplasma spots on a

specimen has been performed by this method of observation. In this sample, occurrence of microplasma has been observed five times as shown in Fig. 19 and Fig. 20. It is noticed that the microplasma No. 1 and No. 2 can not be separated by this method. The same is true for No. 4 and No. 5. Since the diameter of the chopped light spot is approximately 70 microns, it can not necessarily be

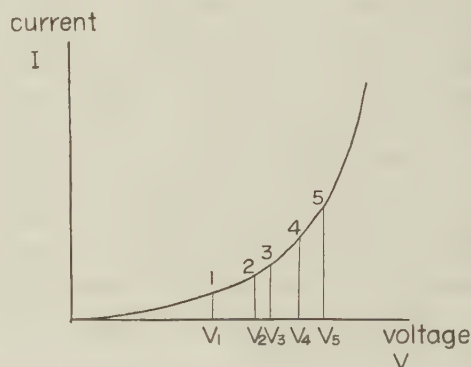


Fig. 19. Current-voltage characteristic of a specimen. Microplasma pulses occur five times in this specimen.

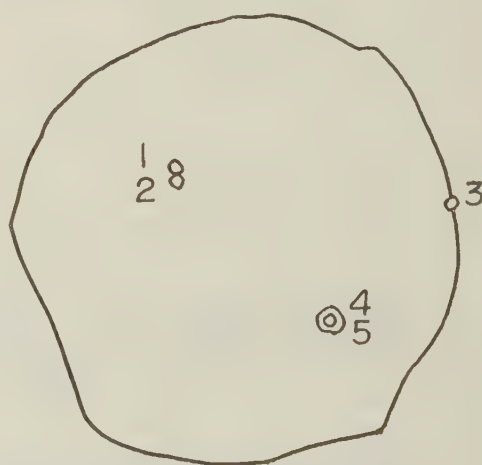


Fig. 20. Located position of microplasma spots in the specimen.

concluded that these pairs of microplasma spots are identical points, respectively. However, it may well be considered that No. 1 and No. 2, or No. 4 and No. 5 are closely correlated as has already been noticed by Champlin¹².

3.5 Measurement of the light output

Total light output from the junction has been measured by the experimental arrangements shown in Fig. 2(b) using photomulti-

plier tube. In the case of Ag-paste electrode experiments, remarkable creeping phenomenon has been found both in the current I and the light output I_p as shown in Fig. 21. Although the variation of I and I_p appears nearly in parallel, the efficiency of light output (i.e., I_p/I) is gradually reduced for prolonged measurement.

In the case of diffused p - n junction, however, the measurement can be performed with much higher reproducibility. The typical re-

sult is shown in Fig. 22. in which experimental points taken with increasing and decreasing voltage are showing fair agreement. In Fig. 23, junction current I and the light output I_p (i.e., the photomultiplier current) are shown as functions of reverse voltage. It may be concluded that the light emission phenomenon is accompanied with the onset of the pre-breakdown current. It is seen in Fig. 22 that the curve does not come to the origin for zero junction current. This can be attributed to the noise (or the dark current) in the photomultiplier.

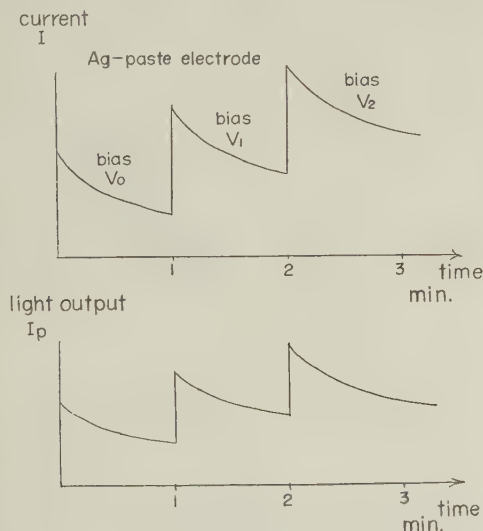


Fig. 21. Creeping effect in the current I and light output I_p observed in the case of Ag-paste electrode on silicon.

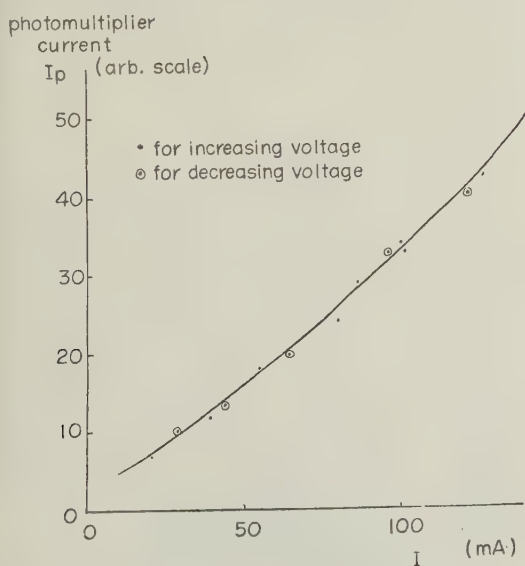


Fig. 22. Relation of light output I_p and the junction current I for diffused p - n junction.

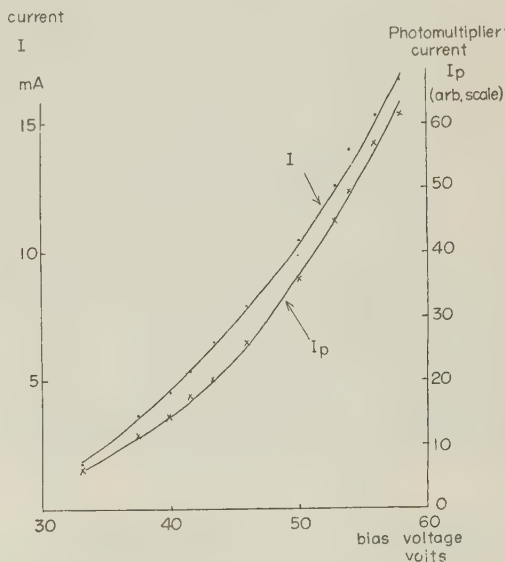


Fig. 23. Junction current I and light output I_p as functions of bias voltage.

3.6 Microplasma pulses and the light emission

As previously mentioned, in the case of Ag-paste electrode experiments, it has been observed that the appearance of the microplasma pulses and the light emitting spots are closely correlated. These two phenomena appear at the jump in the current-voltage characteristic as shown in Fig. 16(a).

It may be quite natural to expect also for the case of diffused p - n junction that the light emitting spot will appear just at the reverse voltage where the microplasma pulses occur.

Our first experiment to detect this possibility has been performed as follows. The occurrence of microplasma is counted with increasing bias voltage, watching the pattern on the synchroscope as shown in Fig. 14. For ex-

ample, occurrence of microplasma is counted five times with increasing voltage up to 43 volts. The surface of the junction is next inspected with microscope to count the light emitting spots. It has turned out that only one light emitting spot is found in the case of above mentioned specimen. In most cases, very poor correlation can be found between the count of microplasma and light spots.

In the above experiment, the discrepancy might be attributed to the possibility that the light is absorbed in the surface layer. Therefore, the next experiment has been devised.

The reverse bias voltage is increased until at least one light emitting spot is observed clearly on the surface. Then, fixing the voltage, small chopped light spot is moved to coincided to the light emitting spot under the the microscope. If really this light emitting spot is the microplasma spot itself, the pattern just like that shown in Fig. 18(c) must be observed on synchroscope provided that the bias voltage is slightly decreased from the fixed value. Contrary to this expectation, the characteristic pattern cannot be observed at the light emitting spot. It has also been confirmed that the pattern is observed when the chopped light is located at somewhere in the "dark" region on the junction surface.

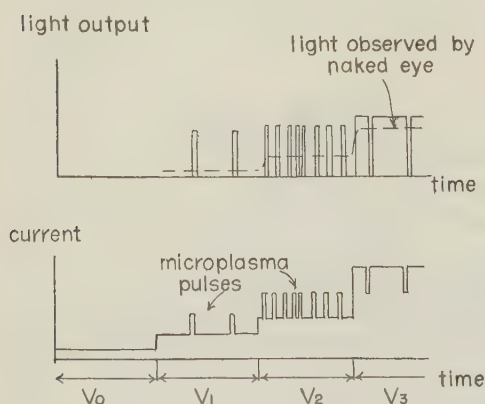


Fig. 24. Speculation of the relation between the current pulse and light output.

Another experiment has been devised from different point of view. As is shown in Fig. 24, our first speculation is that individual current pulse corresponds to the pulsive light output. In the observation of light output by naked eye through microscope or by dc ammeter in the photomultiplier circuit, it may

be considered that the pulsive light output is averaged with the time constants of these systems.

A double beam synchroscope has been used to pick up the microplasma pulses and the light output pulses simultaneously. Unfortunately, no pulse signal could be observed in the light output. Therefore, the signals were fed into x - and y -axes, respectively, only for detecting the correlation between them. The pattern on the synchroscope will be like that shown in Fig. 25(b) if any degree of correlation exists between these two signals.

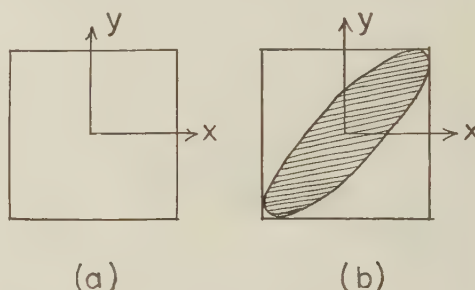


Fig. 25. If two signals are partially correlated, the pattern will become as shown in (b).

No correlation could be found between microplasma pulses and light output signal in our experiment. Although this result may partly be attributed to the lack of sensitivity of photomultiplier system to detect the light output from single light spot, but it may well be considered to be an independent evidence for the previously mentioned experimental results.

§ 4. Discussion

4.1 Carrier multiplication

The effect of carrier multiplication in the voltage range where the microplasma phenomenon is observed must be re-considered on the basis of bistable switching action of the microplasma spot. It has been noticed that the carrier multiplication is not remarkably changed at those voltages, whereas the "apparent" multiplication takes its maximum through the occurrence of microplasma pulses. A typical result is shown in Fig. 26 and the schematic representation is given in Fig. 27. The light is chopped at 225 cps and the current is observed on Iwasaki No. 5301 synchroscope. Fixing the chopped light spot on the microplasma spot as mentioned in 3.4, bias

voltage is gradually increased.

As shown in Fig. 27(a), for the bias voltage lower than the value for the occurrence of microplasma pulses, normal photocurrent r_p is observed. Therefore, the current

$$i_{a0} + r_p, \tag{1}$$

flows in the period of illumination, where i_{a0} is the dark current. As the voltage is increased, however, microplasma pulses become to appear both in the dark and illuminated periods. The pulse rate is much higher in the illuminated condition than in the dark, whereas the pulse height h_m is almost the same. Hence, for the further increase in bias voltage, it becomes to the situation as shown in (c) and (d) of the figure, where the current

$$i_{a0} + r_p + h_m, \tag{2}$$

flows under illumination, the dark current being kept at i_{a0} . In this case, "apparent" photocurrent is $(r_p + h_m)$ which differs h_m from

the usually defined photocurrent r_p .

When the bias voltage is further increased, both the pulse width and pulse rates are so increased that the current stays at the level

$$i_{a0} + h_m, \tag{3}$$

in the dark. (It is noticed that, strictly speaking, h_m in Eq. (3) is different from that in

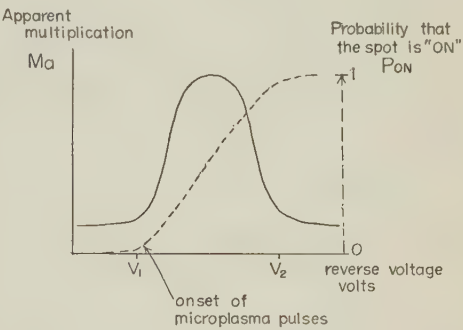


Fig. 28. Apparent multiplication M_a and P_{ON} as functions of bias voltage.

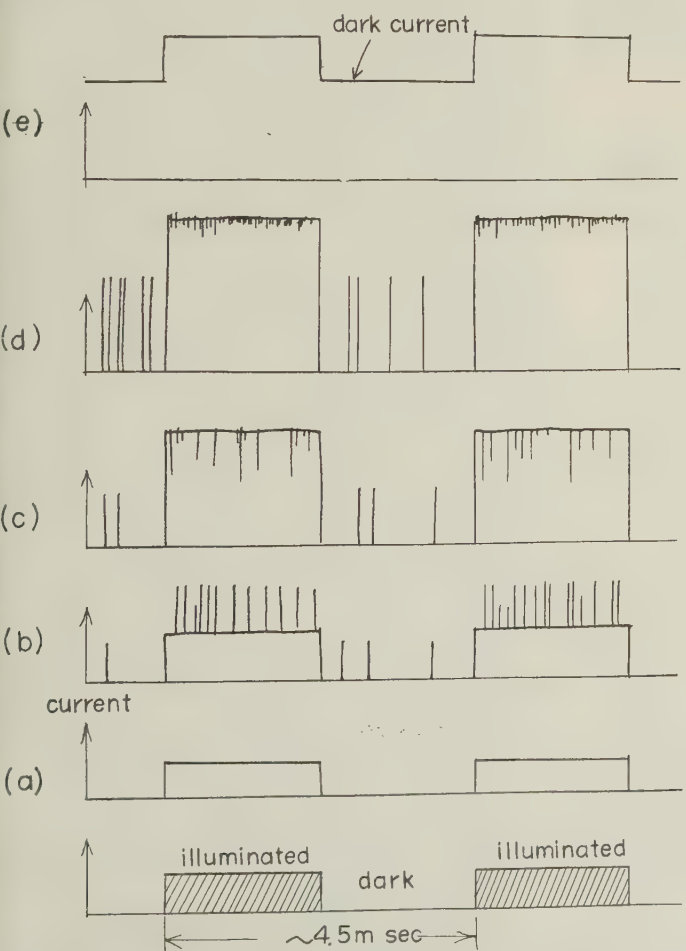


Fig. 27. Schematic representation of Fig. 26.

Eq. (2). However, since h_m 's are greater than or at least comparable to r_p , the dependence of h_m on the bias voltage may be neglected in this discussion.) Hence, the photocurrent is reduced again as shown in Fig. 27 (e).

As mentioned above, apparent carrier multiplication and the microplasma pulse are closely correlated. If we define P_{ON} as the probability of the microplasma spot to be in the state "ON", apparent carrier multiplication M_a and P_{ON} are schematically shown as functions of bias voltage in Fig. 28. M_a starts to increase at the voltage where the onset of microplasma pulses is observed, and it takes maximum at the voltage where P_{ON} takes the value $\frac{1}{2}$. As the voltage is further increased, P_{ON} reaches to unity and M_a is reduced again to certain value.

It has been expected before the experiment that carrier multiplication would take high value after the microplasma spot was switched on (i.e., P_{ON} becomes

to unity), but as is seen in Figs. 26 and 27, this has been found not to be the case. The decrease of M_a for higher bias voltage (Fig. 28) may partly be attributed to the reduction of the impedance which results in the reduction of photocurrent signal, but this cannot be the essential factor, since the junction impedance as a whole is not so changed by the occurrence of the microplasma pulses, and moreover, the similar feature as shown in Fig. 28 can be observed for the microplasma which successively appear with increasing bias voltage.

4.2 Visible light emission and microplasma pulses

As previously touched in 3.6, correlation between the visible light emission and microplasma phenomena must be suspected. We have, in fact, expected that visible light is emitted continually after the microplasma switching spot is turned on. However, this expectation seems now to be denied by the considerations on the basis of experimental results as follows.

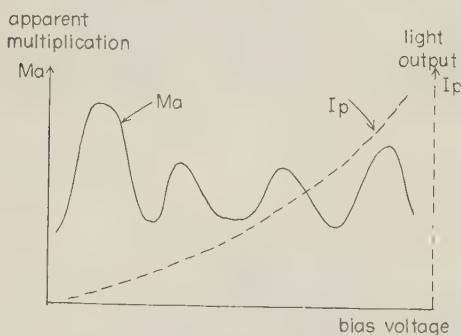


Fig. 29. Dependence of multiplication M_a and light output I_p on bias voltage.

(a) By the experimental result of Chynoweth, et al., it has been estimated that the light is emitted by the transition of high energy electrons and holes which are accelerated by the electric field in the space charge region. As shown in Fig. 29, however, we have observed that the multiplication shows local maxima with increasing bias voltage, whereas averaged light output is increased monotonically. If light emission is really accompanied with high energy carriers in microplasma, it should be expected that M_a is not decreased again in Fig. 28.

(b) As mentioned in 3.6, microplasma pulses can not be found at light emitting spot.

Moreover, visible light emission can not necessarily be observed at microplasma spot.

(c) Although it might be attributed to the lack of sensitivity of photomultiplier tube, unsuccess of detecting correlation between microplasma pulses and light output (mentioned in 3.6) may well serve as an evidence for the lack of correlation itself.

4.3 Mechanism underlying the light emission

As pointed out by Chynoweth, et al.¹⁴⁾, one of the most characteristic features of the light emitting phenomenon is the spectral distribution of emitted light. It has been reported that the spectrum of the light extended far beyond the wavelength corresponding to the band gap of silicon (i.e., 1.2 eV). From this experimental result, it has been concluded that photons of energy substantially less than the gap width are being emitted in the breakdown mechanism.

To account for this it seemed most likely that radiative intraband transitions by energetic electrons and holes are occurring.

There remains some doubt, however, in adopting this physical picture, since we have experimental results as mentioned below.

The visible light emission phenomenon has been reported by several authors, but all are about silicon p - n junctions and none has been reported on germanium. If the inter- and intraband transitions of energetic electrons and holes are the main processes for the light emission, it should well be expected that the similar phenomenon can be observed also in germanium p - n junctions. Of course, this may be a speculation since we have little information about the transition probability functions and the distribution functions for both electrons and holes in germanium, but the lack of information itself cannot depreciate the speculation.

We have tried to account for the difference between silicon and germanium in finding light emission phenomenon on the basis of the difference in extrinsic properties, i.e., the content of oxygen. In the crystals pulled by usual technique, much higher density of oxygen can be found in silicon than in germanium since quartz crucible is inevitably used in the case of silicon.

If oxygen impurity plays some essential role in the light emission, the phenomenon may be expected to occur in germanium p - n

junction containing high density of oxygen. Recently, we have succeeded in observing light spots on germanium diffused $p-n$ junction¹⁵⁾. Germanium crystal used in this experiment was pulled from the melt had been previously heated up to 1400°C in quartz crucible. This success in observing the visible light emission from germanium $p-n$ junction provides an evidence for the effect of oxygen impurity on the light emission phenomenon.

The precise mechanism of the action of impurity atoms is not well understood at present, but it may be considered from two different points of view, i.e.,

- (a) for supplying initial energenic carriers,
- (b) for the emission of photons.

As for the case (a), it may be imagined that some kinds of deep levels provided by oxygen atoms help Zeener effect. In this case, high energy electrons can be supplied much easier for the same electric field intensity. It may also be imagined that the impact ionization of deep-lying levels supplies carriers to cause the electron avalanche.

As for the case (b), it may be considered that inter- and intra-band transition of energetic carriers are caused by the interaction between high energy electrons of holes and oxygen impurities.

The effect of impurity atoms such as oxygen on the light emission may be speculated from another point of view. It is clearly observed that light emission is correlated with the backward leakage current in $p-n$ junction. The non-saturation current component in the backward characteristic of $p-n$ junction has been correlated with deep-lying levels in the space charge region¹⁶⁾. On the other hand, effect of oxygen atoms on the lifetime of minority carriers and backward leakage current are reported by several authors. Especially, it is quite natural to believe the correlation between the "traps"¹⁷⁾ and oxygen impurities from our present knowledge on the crystal pulling technique and the behavior of oxygen in silicon crystals.

Although we have not succeeded in observing one-to-one correspondence between the light emitting spot and dislocation etch pit, light spots could be found along the scratch line on the junction surface. It seems likely that the precipitation of oxygen atoms on the dislocation by Cottrell atmosphere can not be

neglected.

4.4 Switching action of microplasma spot

As is shown in Fig. 28, after the microplasma spot is turned on, no appreciable carrier multiplication is observed. In other words, local electric field in the microplasma spot is reduced in "ON" condition to low value which is insufficient to cause carrier multiplication. This feature reminds us of the characteristics of semiconductor switches such as of $p-n-p-n$ structure. In those kinds of devices, triggering to "ON" condition is performed through the occurrence of avalanche breakdown in the middle junction, but when the turning-on is finished, the middle junction is biased slightly in forward and no avalanche effect is maintained.

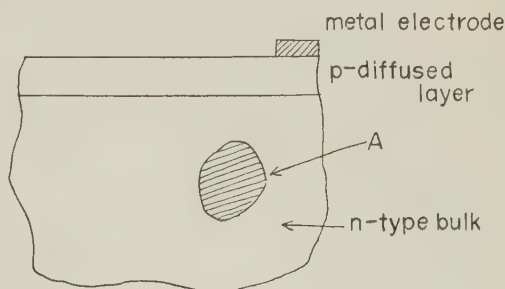


Fig. 30. A proposed model for microplasma spot.

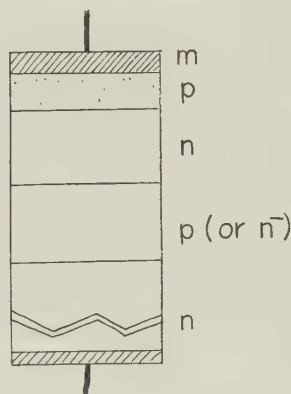


Fig. 31. Structure of microplasma spot.

From the analogy to the $p-n-p-n$ switches, a model as shown in Fig. 30 may be proposed. If a small spot A acts as a hole emitting source, the small part of the junction may be considered as a structure shown in Fig. 31, which corresponds to $p-n-p-n$ switch (m stands for metal electrode). Since the electron emitting efficiency of metal electrode is very low, switching action of this

part is essentially determined by the hole emission from the source *A*. Apparent switching action is expected to be poor because of this structure and the ohmic spreading resistance.

The physical nature of the emitting source *A* is not known at present, but several models are speculated. For instance, a cluster of oxygen impurities, or some kind of crystal imperfections may affect the local electrostatic potential to make such kind of hole emitting source.

From this model, it may be concluded that the light emission will not be observed at this spot, but on the contrary it may be expected that no hole emitting source such as shown in Fig. 30 will be found at the light emitting spot. In the case of light emitting spot, some kind of imperfection is necessary in the junction for the breakdown to occur, but hole emitting spot as shown in Fig. 30 must not exist near that imperfection since high electric field intensity must be sustained for providing high energy electrons and holes in the space charge region.

Some additional information will be found about the above mentioned models in the near future since several experiments are now being devised.

§ 5. Conclusion

By virtue of the light scanning method, it has been found that the microplasma spot can be located on the diffused junction plane, and also that the light emitting spot does not necessarily coincide with the microplasma spot.

It has been found possible that visible light emission phenomenon is essentially affected by the impurity atoms in the crystal, especially with oxygen impurities.

It is noticed that the apparent carrier multiplication is reduced again after the microplasma spot is turned on, from which a model has been proposed taking small hole emitting region into account.

In conclusion, it seems likely that the light emitting phenomenon and the microplasma phenomenon appear at different spots in a *p-n* junction with different underlying mechanisms.

References

- 1) A. G. Chynoweth, et al.: Phys. Rev. **102** (1956) 369. R. Newman: Phys. Rev. **100** (1959) 700.
- 2) A. G. Chynoweth, et al.: J. Appl. Phys. **29** (1958) 1103.
- 3) K. G. McKay: Phys. Rev. **94** (1954) 877.
- 4) F. W. G. Rose: Phys. Rev. **105** (1957) 413.
- 5) A. G. Chynoweth, et al.: Phys. Rev. **102** (1956) 369.
- 6) To be published in J. Phys. Soc. Japan.
- 7) Some of the experimental results have been reported in J. Phys. Soc. Japan **14** (1959) 682.
- 8) W. C. Dash: J. Appl. Phys. **27** (1956) 1193.
- 9) A. G. Chynoweth, et al.: Phys. Rev. **102** (1956) 259.
- 10) K. S. Champlin: J. Appl. Phys. **30** (1959) 1039.
- 11) A part of results has been reported at the meeting of Physical Society of Japan held in April in 1959.
- 12) See ref. 10).
- 13) A. G. Chynoweth, et al.: Phys. Rev. **102** (1956) 369. A. G. Chynoweth, et al.: J. Appl. Phys. **29** (1958) 1103.
- 14) A. G. Chynoweth, et al.: Phys. Rev. **102** (1956) 369.
- 15) To be published in J. Phys. Soc. Japan.
- 16) A. Sah, et al.: Proc. Inst. Radio Engrs. **45** (1957) 1228.
- 17) J. R. Haynes, et al.: Phys. Rev. **100** (1955) 311, 606.

A Possible Mode of Twin in the ϵ -phase of Cu-Sb Alloy*

By Michiyasu Doi

*Section of Metal Physics, Instituto de Pesquisas Tecnológicas,
University of São Paulo, São Paulo, Brazil*

(Received December 17, 1959)

The author found only one symmetry plane ($\bar{1}\bar{2}10$) in the superlattice of the ϵ -phase of Cu-Sb alloy, where an ideal distribution of 8 Sb atoms³⁾ was assumed in the unit cell. This symmetry plane coincides with the plane of shear and is normal to the twinning plane ($10\bar{1}1$), of the twin which was predicted in a hexagonal lattice with the axial ratio, 0.7947, in a previous paper¹⁾. Thus, the author assumed the ($10\bar{1}1$) twin in the ϵ -phase, and discussed atom movements in the twinning. The possibility of detectable twins of this type seems so small that it may be 1/6 (or less) of the possibility for the $\{10\bar{1}2\}$ twin in common h.c.p. metals.

R. W. Cahn has confirmed that no twin can form in an ordered Fe_3Al crystal. Based on this, the author assumed some geometrical requisitions for the twinning of superlattices.

§ 1. Introduction

In a previous paper¹⁾, the author predicted that, if any twin can form in a hexagonal lattice with the axial ratio $c/a=0.795$, the twinning indices will be $K_1=(10\bar{1}1)$, $K_2=(10\bar{1}\bar{1})$, $\eta_1=[\bar{1}012]$ and $\eta_2=[10\bar{1}2]$, and the plane of shear will be ($\bar{1}\bar{2}10$).

Now, it has been reported that the ϵ -phase of Cu-Sb alloy has an approximately hexagonal close-packed superlattice having the $c/a=0.7947$. Accordingly, the author will geometrically discuss the possibility of the formation of the predicted twin in this alloy.

§ 2. Atomic Arrangements in an Unit Cell of the ϵ -phase of Cu-Sb Alloy

Osawa and Shibata²⁾ have studied the ϵ -phase of Cu-30.52%Sb alloy, and measured the lattice parameters that $a_2=10.836 \text{ \AA}$, $c_2=8.611_2 \text{ \AA}$ and $c_2/a_2=0.794_7$. Calculating from the specific gravity measured, they have also concluded that the unit cell contains 45 Cu atoms and 9 Sb atoms. It was then concluded that (1) the ϵ -phase has an unit cell quadrupling of the a -axis and doubling of the c -axis of a simple hexagonal close-packed cell having the parameters $a=2.709_0 \text{ \AA}$, $c=4.305_6 \text{ \AA}$ and $c/a=1.589_4$ (it is called a component cell hereafter); (2) if the ϵ -phase lattice had an ideal hexagonal close-packing, the unit cell would

contain 64 atoms; on the contrary, the net number of atoms contained is only 54, and thus, the lattice is not an ideal hexagonal close-packed one but is very near to it.

Recently, Boettcher and Thun³⁾ have observed an well-defined X-ray diffraction line of superlattice of the ϵ -phase, the interplanar spacing of which being $3.16 \text{ \AA}$. And they have supposed an ideal distribution of 8 Sb atoms in the superlattice cell.

In Fig. 1, these Sb atoms are ordered in a set of $(0\bar{2}\bar{2}2)_2$ planes, where the subscript " ϵ " denotes the indices referred to the whole unit cell with the $c_2/a_2=0.794_7$. The superlattice apparently arises from the homopolar portion of the binding forces of Sb atoms, the distance between them being enlarged to $3.82 \text{ \AA}$.

The superlattice cell certainly contains more than 8 Sb atoms. They have then supposed that Sb atoms in excess may probably lie in the planes parallel to the basal plane either at heights $c/2$ and c , or at heights $c/4$ and $3c/4$.

Moreover, the superlattice cell contains only 54 atoms, which is considerably less than 64 atoms for closest-packing. Thus, they have assumed that the vacant lattice sites involved may take an ordered arrangement in, for example, the $(20\bar{2}2)_2$ planes, which lie alternately with the $(10\bar{1}1)_2$ planes occupied by Sb atoms, as shown in Fig. 1. However, the correct positions of the vacancies remain still unknown.

* This paper was expressed at the 14th Congress of Associação Brasileira de Metais, July 1959 at Belo Horizonte, Brazil.

($10\bar{1}2$), in Cd. Fig. 3 shows this arrangement, which is obtained by the procedure that the two half-lattices are subjected to one or two minor readjustments of atomic sites near the common plane, ($10\bar{1}2$), in order to establish the symmetry of the twin boundary and to relieve the more obvious misfits.

If the above arrangement of atoms were to be realized, the Sb atoms would come into the same twin interface, as seen in Fig. 2; in consequence, the ordering and bonding of atoms would undergo any changes at the twin boundary. Can such local structural irregularities be tolerated in the twinning of some electron compounds, such as the ϵ -phase of Cu-Sb alloy which is in ordered state throughout the whole range of temperature?

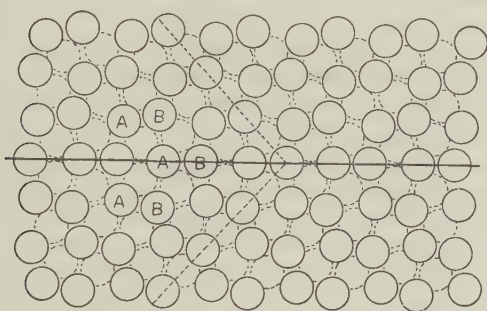


Fig. 3. An arrangement of atoms at a twinning plane in a hexagonal close-packed Cd lattice. A heavy line shows trace of the twinning plane ($10\bar{1}2$), and dashed lines traces of basal planes in the plane of shear ($1\bar{2}10$) represented by the plane of the paper. (After Thompson and Millard⁴)

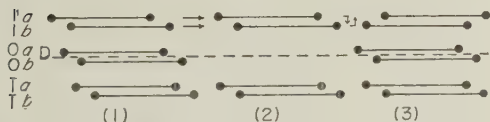


Fig. 4. Interchange mechanism and final arrangement of atoms in the twinning of multiple lattices consisting of the pairs of planes separated by narrow gap. A dotted line shows a hypothetical twin interface. (After Jaswon and Dove⁵)

Jaswon and Dove⁵ have suggested an alternative arrangement of atoms at a twin boundary in multiple lattices, e.g. hexagonal close-packed lattice. Fig. 4 shows this arrangement, where the twin interface, as indicated by a dotted line, is the hypothetical plane of imagined mirror midway between the pair of planes O_a and O_b separated by narrow gap.

After twinning, the planes O_a and O_b have moved toward compromise positions between matrix and twin, but the equilibrium stacking of these planes is largely maintained. Thus, the energy of twin boundary may be mainly ascribed to the misfits between the widely spaced neighbouring planes O_b , $\bar{1}a$ and O_a , $1b$, as suggested by them.

The above arrangement of atoms at a twin boundary seems more realizable in the twinning of the ϵ -phase than that shown in Fig. 3, because the ordered state may almost be maintained at the twin boundary.

§ 4. Discussions

In the preceding section, the author suggested a possible mode of twin in the ϵ -phase of Cu-Sb alloy, by assuming an ideal distribution of 8 Sb atoms in the unit cell, as suggested by Boettcher and Thun³.

As described in § 2, the actual unit cell can contain 9 Sb atoms, and thus, minor adjustment must be carried out for the arrangement of atoms and their movements in the twinning. Moreover, the unit cell contains vacant lattice sites, although their correct positions remain still unknown. The author, then, did not consider the vacancies in the present paper.

We shall next consider the possibility of detectable twins of this type. As described in § 2, only the ($1\bar{2}10$)_ε plane is a symmetry plane among three { $1\bar{2}10$ }_ε planes. In addition, only the ($10\bar{1}1$)_ε plane can become a twinning plane, among the { $10\bar{1}1$ }_ε planes normal to the plane of shear, ($1\bar{2}10$)_ε, as seen in Fig. 2.

On the other hand, the { $10\bar{1}2$ } twin can form in hexagonal metals with the axial ratios less than $\sqrt{3}$, only when strained in a direction near to the c -axis, as pointed out by Schmid and Boas¹⁶.

Considering the above restrictions, the suggested twin seems so difficult to detect that the possibility of formation may be 1/6 (or less) of the possibility for the { $10\bar{1}2$ } twin in common hexagonal close-packed metals.

Finally, we shall discuss the formation of twin in an ordered Fe₃Al crystal. As this alloy has body-centred cubic structure, we shall here consider only the {112} twin.

R. W. Cahn has confirmed that no twin

can form in this superlattice. The fact seems to suggest the geometrical condition which must be satisfied in the twinning of superlattices, that is, the necessary symmetry of twin boundary is established for all kinds of component atoms. Fig. 5 shows that the above condition can not be established in this superlattice.

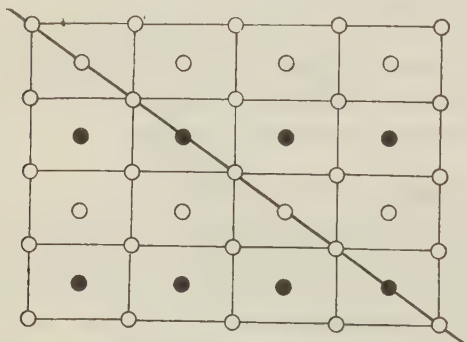


Fig. 5. A projection of atoms in the $(\bar{1}10)$ plane of an ordered Fe_3Al crystal. Open and closed circles show Fe and Al atoms, respectively; a heavy line shows trace of the (112) plane.

An alternative reason supposed is this: the ordering and bonding of atoms may undergo any changes at the twin boundary, and it is likely that such structural irregularities are intolerably large in the twinning of large shear. This supposition, however, must be

proved in an ordered FeAl alloy, in the twinning of which the above symmetry requisition is established.

On the contrary, the twin supposed in the ϵ -phase of Cu-Sb alloy involves a small shear, 0.172, which is comparable to that of the $\{10\bar{1}2\}$ twin in Zr. It should be noted that the ϵ -phase involves bonding of a partly homopolar nature, contrary to the superlattices of Fe-Al alloys.

Acknowledgement

The author wishes to express his gratitude to the Instituto de Pesquisas Tecnológicas de São Paulo, Brazil, for support of the work; to Eng^o Jorge A. Cintra for his help and advice.

References

- 1) M. Doi: Boletim da Associação Brasileira de Metais **15** (1959) 655.
- 2) A. Osawa and N. Shibata: Sci. Repts. Tohoku Imp. Univ. **28** (1939) 1.
- 3) A. Boettcher and R. Thun: Z. anorg. Chem. **283** (1956) 26.
- 4) N. Thompson and D. J. Millard: Phil. Mag. **43** (1952) 422.
- 5) M. A. Jaswon and D. B. Dove: Acta Cryst. **9** (1956) 621; **10** (1957) 14.
- 6) E. Schmid and V. Boas: *Plasticity of Crystals* (1935); English Translation, F. A. Hughier and Co. Ltd. London (1950) 96.

Shape of Nucleus Domain Anchored to a Screw Dislocation in Ferroelectric Crystal*

By Hidetosi TAKAHASI,

*Department of Physics, Faculty of Science
University of Tokyo*

Terutaro NAKAMURA,

*Department of Physics, Faculty of Science
Ochanomizu University, Otsuka, Tokyo*

and Yoshihiro ISHIBASHI

*Department of Physics, Faculty of Science
University of Tokyo*

(Received January 9, 1960)

The elastic deformation around a screw dislocation in a ferroelectric crystal, which has a spontaneous shear strain in ferroelectric state was solved using the relaxation method, taking into account the nonlinear stress-strain relationship of the ferroelectrics. The result turned out to contain a discontinuity corresponding to the domain boundary. This domain is plate-like in the absence of the external field but becomes wedge-shaped by application of a field. The relaxation process is analogous to the one used in solving ordinary Laplace equation but differs in that the stress is put to zero when the strain is less than a certain magnitude. The calculation took a few hours on a digital computer PC-1.

§1. Introduction

It is widely believed that an important mechanism of the polarization reversal of ferroelectric crystals is the nucleation of reversed domains. One of the authors¹⁾ pointed out that the mechanism of domain nucleations and of sticking of domain walls during wall motion is intimately related to crystal imperfections. The type of imperfection to be considered is a dislocation line which would have been produced in the crystal during the crystallization process, and it was shown that a small cylindrical domain is anchored to each dislocation line, and could act as a nucleus of a reversed domain. It is known that, when heated above the Curie point and cooled down, ferroelectric crystals tend to assume domain patterns similar to those before heating, and also that domain switching in a crystal starts at certain definite sites each time an electric field is applied. These phenomena will be reasonably understood if

small cylindrical domains are held up by dislocations.

The present paper is an attempt to determine theoretically the exact shape of the small domain held up by each dislocation line. The problem involves the solution of equation of elasticity assuming an idealized stress-strain relation of the ferroelectric crystal. This is done by a rather straightforward manner by applying the relaxation technique to the solution of a nonlinear partial differential equation. While the work is exploratory and is done for a somewhat simplified model, it may be extended to many similar situations involving the relation of nonlinear equations.

§2. Mathematical Model

For the calculation, let us consider a simplified mathematical model, in which the crystal has stress-strain characteristic curves as shown in Fig. 1.

Strain y_z has a finite value $\pm y_z^s$ even when Y_z is zero. This strain y_z^s is called spontaneous deformation. For the nonvanishing values of Y_z the relation

* The whole computation in this work was made by a digital computer PC-1, built under the direction of one of the authors and installed in the Department of Physics, University of Tokyo.

$$y_z = \frac{1}{c_{44}^p} Y_z \pm y_z^s \tag{2.1}$$

is satisfied. Relation between Z_x and z_x is normal, i.e.,

$$z_x = \frac{1}{c_{55}^p} Z_x \tag{2.2}$$

A relation

$$c_{44}^p = c_{55}^p \tag{2.3}$$

is also satisfied.

As far as the screw dislocation parallel to z -axis is concerned, the only nonvanishing component of displacement (u, v, w) is the z -component w . Hence it is not necessary to consider other stresses or strains than Y_z, Z_x, y_z and z_x .

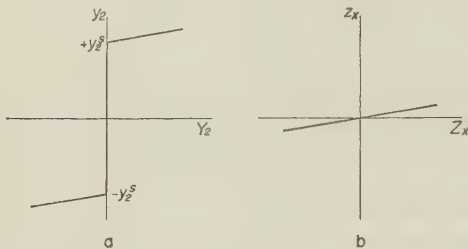


Fig. 1. Stress-strain characteristic.

The present model has been adopted bearing in mind the image of rochelle salt crystal, which differs from the present model only in the point that $c_{44}^p \neq c_{55}^p$. In a qualitative discussion, however, the assumption $c_{44}^p = c_{55}^p$ will not give any important influence on the conclusion.

§ 3. Method of Calculation

In the following discussions we only deal with a two-dimensional problem in x - y plane. The method is essentially identical with the ordinary relaxation method as applied to solution of Laplace equations except that the equation to be solved is nonlinear.

Since the stress-strain curve of our crystal is assumed to be as shown in Fig. 1, it is readily seen that in the region, where $|y_z| \geq y_z^s$, $y_z - Y_z$ characteristic is linear and the solution is identical with the case of ordinary elastic material. In other words, except in the region including ferroelectric domain wall, the present problem reduces to that of solving a linear equation:

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = 0 \tag{3.1}$$

under suitable boundary conditions.*

On the other hand, for values of y_z that satisfies $|y_z| < y_z^s$, it is seen from Fig. 1(a) that stress Y_z is zero. This is equivalent to assuming that the regions on both sides of a domain wall do not affect any interactive forces to each other.

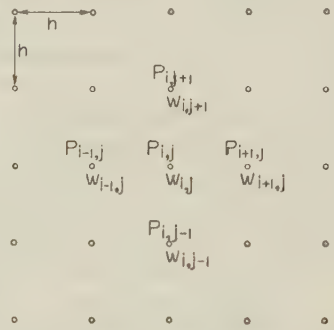


Fig. 2. Square lattice representing x - y plane.

For calculation using a digital computer, the x - y plane of the crystal is represented by an assembly of lattice points $P_{i,j}$ of square lattice, of which lattice spacing is h (Fig. 2). It is to be noted that this lattice does not correspond to the real crystal lattice. As will be given in § 6, the lattice spacing h considered here is much larger than actual atomic lattice spacing.

Let the amount of displacement of the point $P_{i,j}$ in z direction be denoted by $w_{i,j}$, then the difference $(w_{i,j} - w_{i-1,j})/h$ represents the strain component z_x and $(w_{i,j} - w_{i,j-1})/h$ represents the strain component y_z at the respective points in the crystal. In the solution of ordinary Laplacian equation (3.1), the actual equation to be solved is the system of linear algebraic equations:

$$4w_{i,j} = w_{i+1,j} + w_{i-1,j} + w_{i,j+1} + w_{i,j-1} \tag{3.2}$$

Now it is necessary to distinguish whether the considered region includes a domain wall. In the lattice approximation, this amounts to distinguishing whether the domain wall separates the pair of lattice points $(P_{i,j}, P_{i,j-1})$. This distinction is actually made by observing whether the inequality

* Fundamental equation of elasticity for an ordinary elastic material, in which the only non-vanishing component of displacement (u, v, w) is the z -component w , is given by

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = 0 .$$

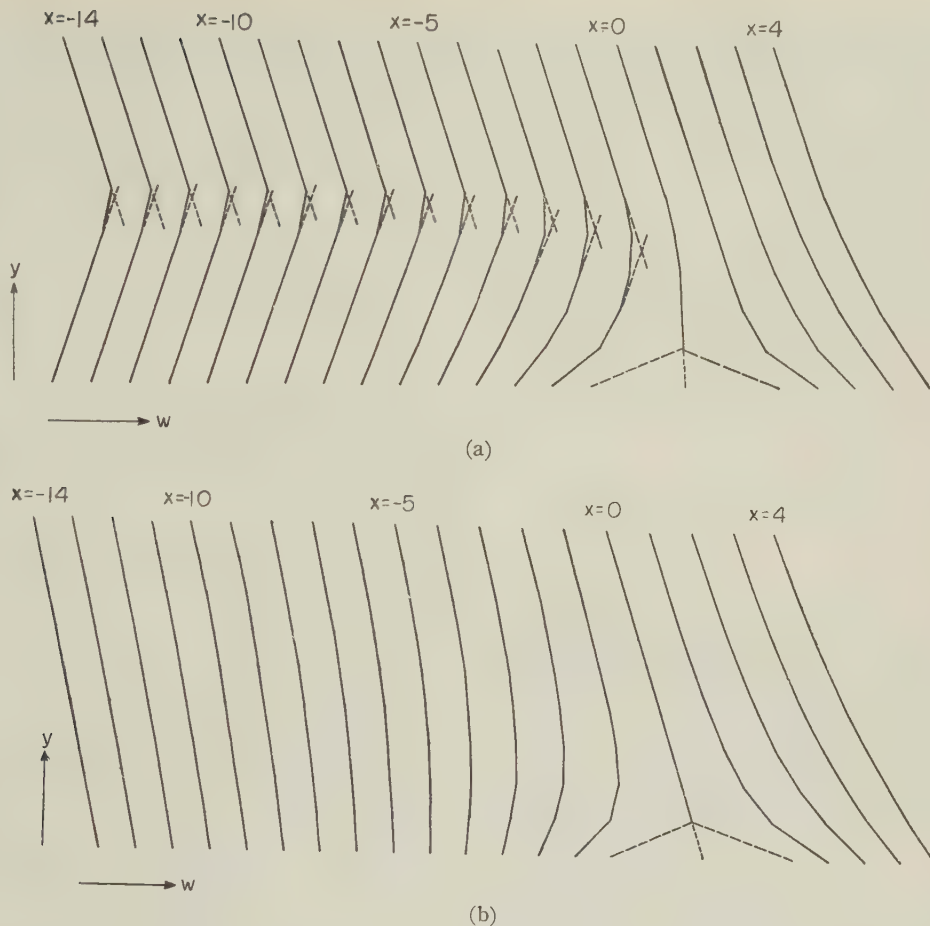


Fig. 3. (a) Displacement $w_{i,j}$ as a function of $y=jh$, for various $x=ih$. (b) Similar figure to Fig. 3a for a crystal, which has a spontaneous strain y_z^s but has a normal stress-strain characteristic.

$$|w_{i,j} - w_{i,j-1}| < hy_z^s \quad (3.3)$$

is satisfied.

If, in the equation like (3.1) involving five neighboring points $P_{i,j}$, $P_{i-1,j}$, $P_{i+1,j}$, $P_{i,j-1}$, $P_{i,j+1}$, neither of the pairs $(P_{i,j}, P_{i,j-1})$ ($P_{i,j}, P_{i,j+1}$) is separated by the domain wall, the partial derivative $\partial^2 w / \partial y^2$ is replaced by finite difference:

$$\begin{aligned} & \frac{1}{h^2} ((w_{i,j+1} - w_{i,j} \mp hy_z^s) - (w_{i,j} - w_{i,j-1} \mp hy_z^s)) \\ &= \frac{1}{h^2} (w_{i,j+1} + w_{i,j-1} - 2w_{i,j}). \end{aligned} \quad (3.4)$$

For $\partial^2 w / \partial x^2$, we obtain the expression:

$$\frac{1}{h^2} (w_{i+1,j} + w_{i-1,j} - 2w_{i,j}) \quad (3.5)$$

which is identical to that for the ordinary Laplacian equation. From (3.4) and (3.5) we obtain the equation:

$$4w_{i,j} = w_{i+1,j} + w_{i-1,j} + w_{i,j+1} + w_{i,j-1} \quad (3.6)$$

which is identical to the ordinary equation (3.2). That is, except in the regions including the domain wall, the replacement of characteristic of Fig. 1(b) by that of Fig. 1(a) does not affect the equation.

Let us next consider the case that the two points $P_{i,j-1}$ and $P_{i,j}$ is separated by the domain wall, that is, the case that

$$|w_{i,j} - w_{i,j-1}| < hy_z^s.$$

Since in this case we assume that the two points $P_{i,j-1}$ and $P_{i,j}$ do not interact with each other, it is most natural to drop the term $w_{i,j} - w_{i,j-1} \mp hy_z^s$ from (3.4), so that we obtain the equation

$$3w_{i,j} = w_{i+1,j} + w_{i-1,j} + w_{i,j+1} \mp hy_z^s. \quad (3.7)$$

For the convenience we rewrite (3.7) as

$$4w_{i,j} = w_{i+1,j} + w_{i-1,j} + w_{i,j+1} + w_{i,j} \mp hy_z^s. \quad (3.8)$$

It will be seen that the equations (3.8) is obtained by substituting $(w_{i,j} \mp hy_z^s)$ for $w_{i,j-1}$ in equation (3.6). Similarly, for the case that the two points $P_{i,j+1}$ and $P_{i,j}$ are separated by the domain wall, by substituting $(w_{i,j} \mp hy_z^s)$ for $w_{i,j+1}$ in equation (3.6), we obtain the equation

$$4w_{i,j} = w_{i+1,j} + w_{i-1,j} + w_{i,j} + w_{i,j-1} \pm hy_z^s. \quad (3.9)$$

Actually these equations are solved by the relaxation method by setting an initial trial solution for $w_{i,j}$ and using equations (3.6), (3.8) and (3.9) as iterative equation to improve the approximation to the solution. That is, we put

$$4w_{i,j}^{(k+1)} = w_{i+1,j}^{(k)} + w_{i-1,j}^{(k)} + w_{i,j+1}^{(k)} + w_{i,j-1}^{(k)} \quad (3.6')$$

$$4w_{i,j}^{(k+1)} = w_{i+1,j}^{(k)} + w_{i-1,j}^{(k)} + w_{i,j+1}^{(k)} + w_{i,j}^{(k)} \mp hy_z^s \quad (3.8')$$

$$4w_{i,j}^{(k+1)} = w_{i+1,j}^{(k)} + w_{i-1,j}^{(k)} + w_{i,j}^{(k)} + w_{i,j-1}^{(k)} \pm hy_z^s \quad (3.9')$$

where $w_{i,j}^{(k)}$ represents the k -th approximation for the real solution $w_{i,j}$ of the equations (3.6), (3.8) and (3.9).

Outside the region including the domain wall these equations are identical to the relaxation equations for the usual Laplacian equation. In the region including the wall, the equations, (3.8'), (3.9') differ from the usual one in two points. First, they contain in the right hand side the term $w_{i,j}^{(k)}$, which is the former approximate value at the point $P_{i,j}$ itself, and second, a constant term $\pm y_z^s h$ is added.

So far, it has not been established that our modified relaxation process based on (3.6'), (3.8') and (3.9') always converges to a stable solution of the equation (3.6), (3.8) and (3.9). This will be shown by the following consideration based on variational principle. The convergence of the ordinary relaxation process using the equation (3.6) results from the fact that the energy expression

$$W = \frac{1}{2h^2} \sum ((w_{i,j} - w_{i,j-1})^2 + (w_{i,j} - w_{i+1,j})^2) \quad (3.10)$$

always decreases in each step of the substitution using (3.6'). The same argument applies to the present case if we use the modified energy expression:

$$W = \frac{1}{h^2} \sum \left(\Phi(w_{i,j} - w_{i,j-1}) + \frac{1}{2}(w_{i,j} - w_{i-1,j})^2 \right) \quad (3.11)$$

where $\Phi(\xi)$ is a function defined by:

$$\Phi(\xi) = \begin{cases} \frac{1}{2}(\xi - hy_z^s)^2 & \text{for } \xi \geq hy_z^s \\ 0 & \text{for } |\xi| < hy_z^s \\ \frac{1}{2}(\xi + hy_z^s)^2 & \text{for } \xi \leq -hy_z^s \end{cases}$$

The equations (3.6), (3.8) and (3.9) are derived from (3.11) by putting $\partial W / \partial w_{i,j} = 0$. If either of the conditions

$$w_{i,j} - w_{i,j-1} \geq hy_z^s, \quad w_{i,j+1} - w_{i,j} \geq hy_z^s$$

or

$$w_{i,j} - w_{i,j-1} \leq -hy_z^s, \quad w_{i,j+1} - w_{i,j} \leq -hy_z^s$$

is satisfied, the expression involving these points is given by (3.4), which is the same as the ordinary expression, while if, for example,

$$-hy_z^s < w_{i,j} - w_{i,j-1} < hy_z^s$$

the term $(w_{i,j} - w_{i,j-1} - hy_z^s)$ in (3.4) drops out and we obtain (3.8).

§ 4. Equation under an Applied Field

Ferroelectric crystals of the type of rochelle salt are "naturally" piezoelectric, that is, piezoelectric even above Curie point, and it is interesting to study the behavior of the anchored domains in such crystals under an applied field. The effect of an applied field on the energy function $\Phi(\xi)$ is given by an additional term* $+d_{14}E_x h^2 \xi$, so that

$$\Phi(\xi) = \begin{cases} \frac{1}{2}(\xi - hy_z^s)^2 + d_{14}E_x h^2 \xi & \text{for } \xi \geq hy_z^s \\ d_{14}E_x h^2 \xi & \text{for } |\xi| < hy_z^s \\ \frac{1}{2}(\xi + hy_z^s)^2 + d_{14}E_x h^2 \xi & \text{for } \xi \leq -hy_z^s \end{cases} \quad (4.1)$$

By substituting (4.1) in (3.11) and differentiating with respect to $w_{i,j}$, we obtain the equation which are quite identical to (3.6), (3.8) and (3.9), the effect of the additional term $+d_{14}E_x h^2 \xi$ being cancelled out in the resultant equation. It will be later shown that the effect of the field comes into play in the boundary condition.

§ 5. Boundary Condition

a) Boundary condition without applied field

Since the actual computation is done for a

* Considering the effect of the applied field, crystal is supposed to be electroded. In this case c_{44}^E and c_{44}^D would take place of c_{44}^P and c_{44}^A in (2.1), (2.2) and (2.3), which would correspond to an isolated crystal. For the isolated crystal, term to be added will be $b_{14}P_x h^2 \xi$.

finite region, it is necessary to put some conditions on the boundary values. In the present calculation the following boundary conditions were used.

(1) On the side $\overline{XX'}$ (Fig. 4a), the displacements are given fixed values, namely:

$$\text{on } \overline{OX}: w=b/2$$

$$\overline{OX'}: w=0$$

where b denotes the amount of Burgers vector, and O denotes the location of a screw dislocation.

(2) The side $\overline{YY'}$ is supposed to be "free", that is, if $P_{i,j+1}$ is a point just outside the boundary, $w_{i,j+1}$ is replaced by $(w_{i,j}-y_z^s h)$ in the right side of the equation determining $w_{i,j}$. The situation is similar to the condition on the domain boundary. The sides XY and $X'Y'$ are also supposed to be free,

that is, $w_{i+1,j}$ for the point just outside the boundary should be replaced by $w_{i,j}$ in the right side of the equation.

b) *Boundary condition under an applied field*

In order to take into account the effect of applied field on the boundary condition, we take the energy expression (4.1) as the basis. By putting this in (3.11) and omitting the term involving $w_{i,j+1}$ in (3.4), we obtain the equation for the boundary point $P_{i,j}$ as

$$\frac{1}{h^2}((w_{i,j-1}-w_{i,j})+h(y_z^s-d_{14}E_xh)) \\ + (w_{i-1,j}-w_{i,j})+(w_{i+1,j}-w_{i,j}))=0$$

or

$$4w_{i,j}=w_{i,j-1}+w_{i+1,j}+w_{i-1,j} \\ +w_{i,j}+h(y_z^s-d_{14}E_xh).$$

§ 6. Result

The following results have been obtained by using PC-1. The calculation took a rather long time, a few hours. The calculation was made using the spacing h in Fig. 2 equal to 2.5×10^{-6} cm. Note that this is far greater than the lattice constants of rochelle salt ($a=11.93$ Å, $b=14.30$ Å, $c=6.17$ Å according to Beevers-Hughes).

a) *Without field applied*

The result in Fig. 3a show the displacement $w_{i,j}$ as a function of $y=jh$, for various $x=ih$. In the left part of the figure, corresponding to negative values of x , the points lie essentially on straight lines of constant positive or negative slope, with a conspicuous break along a line parallel to the x -axis. Since the difference $(w_{i,j}-w_{i,j-1})$ satisfy

$$|w_{i,j}-w_{i,j-1}| < hy_z^s$$

in this part, the domain boundary is supposed to pass between the points $P_{i,j}$ and $P_{i,j-1}$. In this way we obtain the approximate shape of the domain wall as shown in Fig. 4a.

Perhaps one of the interesting features of our calculation is that the formation of a discontinuity corresponding to domain boundaries resulted from "mechanical" solution of the nonlinear equation (3.6), (3.8) and (3.9). Note that the computer has not been "taught" to find a solution having a discontinuity. Shape of the domain seems to be reasonable. Taking the constants for rochelle salt by putting $b=6.17$ Å, $y_z^s=8 \times 10^{-4}$, width of the do-

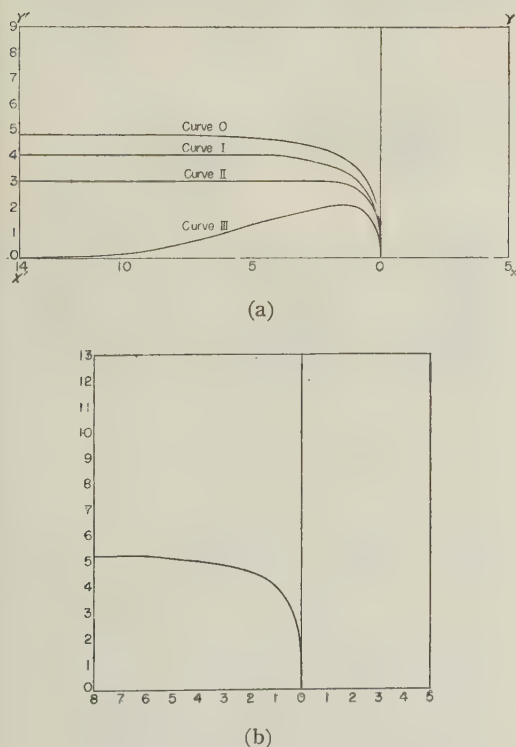


Fig. 4. (a) Shape of domain anchored to a screw dislocation.

Curve O: without applying field.

Curve I, II, III in applying field,

I: $k=0.09$, II: $k=0.143$, III: $k=0.429$,

where

$$k = \frac{d_{14}E_x}{y_z^s}$$

(b) Shape of anchored domain, without field, for another region of calculation.

main anchored to the dislocation is 0.24μ from the curve O in Fig. 4a.

Theoretical consideration indicates that the asymptotic width of the domain anchored to a single screw dislocation in an infinitely large crystal must be

$$2d = \frac{b}{2y_z^s}$$

which is 0.39μ for rochelle salt. The difference between this value and the value obtained from the curve O in Fig. 5a may be due to the finite size of the region over which the equation was solved. Our postulate of the free boundary is equivalent to assuming a periodic two-dimensional array of dislocations of positive and negative senses as shown in Fig. 5. This arrangement of dislocation would cause "image forces", resulting in reduction of domain width.

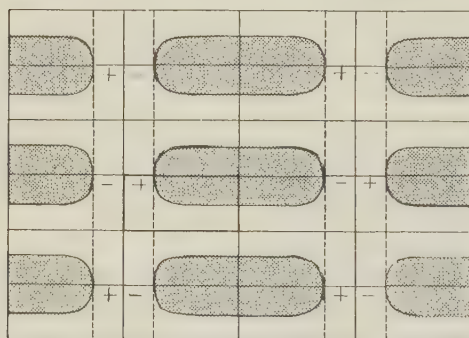


Fig. 5. Distribution of positive and negative dislocations corresponding to the postulate of the "free" boundary.

In order to confirm this view, calculation was made for another arrangement of dislocations, that is, for another form of the region of calculation, as shown in Fig. 4b. The result gave a larger value of 0.26μ , showing a tendency as expected.

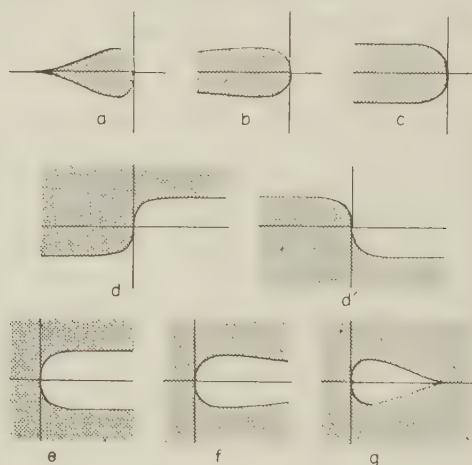
b) With applied field

Curves I, II and III of Fig. 4a show the result of calculation under the boundary condition described in §5 (b). It is seen that the width of the domain decreases with increase of the applied field, until it takes the form of a wedge as shown in curve III of Fig. 4a.

§7. Discussion

From the results of our calculation, which may be considered as a "numerical experi-

ment", we can make the following image for the behavior of domains anchored to a dislocation under varying external field. Suppose that the crystal is in a very high field and is saturated in one direction. In this state, domain anchored to a screw dislocation will be as shown in Fig. 6a. If the field is reduced domain will grow in length and breadth (b and c), until its length becomes infinite when the field is zero. Under the condition of zero field, states shown in c, d, d' and e of Fig. 6 are all equally possible. Hence, when the field is reversed and increased, the state c will change abruptly to e, perhaps through the intermediate state d or d', and "white" domain will shrink through state f down to g.



Figs. 6. Process of growth and shrinking of the nucleus domain.

It will be seen by comparison of a and b of Fig. 3 that the elastic energy of the dislocation is largely "relaxed" by the formation of the domain. It is well known that a two-dimensional array of parallel screw dislocations is not stable because of the elastic interactions. Relaxation of stresses due to the formation of domains would tend to increase the stability of screw dislocations in ferroelectric crystals.

§8. Conclusion

Shape of domain, anchored to a screw dislocation in ferroelectric crystal, which has a spontaneous shear strain y_z^s in ferroelectric state, was calculated using a digital computer. The result turned out to be reasonable.

The calculation was made under the assumption that screw dislocations of positive and negative senses are arranged in a lattice as shown in Fig. 5. The width calculated under this assumption is less than the width of domain in the case that only one dislocation exists in the infinitely large crystal, because of the interaction.

The slope of lattice plane in the nucleus domain is essentially the same as the spontaneous strain.

External applied field causes the deformation and shrinking of the anchored domain.

The calculation is tentative and the precision is not quite satisfactory, but it has at least shown that solution of this sort of non-linear partial differential equation is feasible on an electronic digital computer.

Reference

- 1) T. Nakamura: J. Phys. Soc. Japan **9** (1954) 425; **11** (1956) 624.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

Dynamical Theory of Electron Diffraction in Laue-case, II. Numerical Calculation of Intensities

By Fuminori FUJIMOTO

*Institute of Physics, College of General Education, University of Tokyo
Komaba, Meguro-ku, Tokyo*

(Received January 9, 1960)

The intensities of 111-reflections of Al and Au are calculated by the method of power expansion of the scattering matrix given in the previous paper [J. Phys. Soc. Japan **14** (1959) 1558], and of 333-reflections, by the use of Feynman expansion of the scattering matrix. The results are compared with those given by the two-wave approximation and by the kinematical theory. If we allow an error of 3% in the intensity, the critical thickness of the crystal for 40 kV electrons below which the kinematical theory can safely be applied is 60 Å and 15 Å for Al and for Au, respectively. For higher order reflections such as 333, the deviation of the intensity from those of the two-wave approximation and of the kinematical theory is considerable. It is pointed out that the methods of elimination of the dynamic effect have to be re-examined.

§ 1. Introduction

One of the most difficult problems in the structure analysis of crystals by means of electron diffraction lies in the elimination of the dynamic effect which may affect considerably the intensity of strong reflections. For eliminating this effect, Honjo and Kitamura^{1), 2)} proposed a method to attain the kinematical intensity by extrapolating the measured intensities at various wave-lengths to the zero wave-length limit, and Nagakura³⁾ proposed a method making use of Wilson's intensity statistics. In both of these methods, the intensity formula developed by Blackman⁴⁾

based upon the two-wave approximation was assumed. Recent examinations of the dynamical theory, however, show that the systematic interactions play an important role in the intensity of reflections⁵⁾. Therefore, the theoretical basis of the above two methods should be re-examined taking account of the interactions among many reflected waves, especially of the systematic interactions.

The author has presented, in a previous paper^{6)*}, a general formulation of the dy-

* In the following, Part I is referred to as I. Equations and sections in Part I are cited by adding I, such as (10-I) and Section 2-I.

namical theory, and has obtained the intensity formula which exactly holds in the Laue-case. In the present paper, the approximate calculations taking account of the systematic interactions are given for the 111-reflections from Al and Au by the use of a power expansion of the component of the scattering matrix. As a marked effect of the systematic interactions is expected on higher order reflections* of a strong reflection, the 333-reflections of Al and Au are also calculated by the use of the Feynman expansion⁷⁾, which is powerful in calculating the scattering matrix.

§2. Effect of Weak Waves

The expansion of the scattering matrix in power series of $D/2k$ (D , the thickness of the crystal and k , the mean wave vector in crystal) given in I shows that the intensity tends to the kinematical value for small $D/2k$. However, the convergence of this series is bad when many number of reflected waves have to be taken into account, i.e. when the order of matrix M given by (10-I) is large. Accordingly, it is desirable not to take into account too many reflections in the practical calculation. In the following, we shall discuss how many reflections should be taken into account.

According to the results given in I, the intensity of the h -reflection for real v_h is given by

$$\begin{aligned} I_h &= \sum_{i,j} u_h^i u_h^j \exp \left[i \frac{D}{2k} (x^i - x^j) \right] \\ &= \sum_{i,j} u_h^i u_h^j \cos \left[\frac{D}{2k} (x^i - x^j) \right] \\ &= -2 \sum_{i,j} u_h^i u_h^j \sin^2 \left[\frac{D}{4k} (x^i - x^j) \right], \quad (1) \end{aligned}$$

where u_h^i is the amplitude of the h -wave belonging to the i -th wave field and $x^i/2k$ represents the quantity which is equal to the normal component of the wave vector of the i -th wave field minus a certain constant, so that $(x^i - x^j)/2k$ gives the difference in the normal components of the wave vectors of the i -th and j -th wave fields. The number of

wave fields obtained by solving the fundamental equation of the dynamical theory is equal to the number of reflections considered in the fundamental equation or in the matrix M . We shall denote, in the following, the branches of the dispersion surface as g and g' which lie in the vicinity of the section of the two spheres of radius k , having the reciprocal lattice points G and $H-G$ as centres, respectively (Fig. 1). In this section, we shall deal with the intensity of h -reflection at the Bragg position.

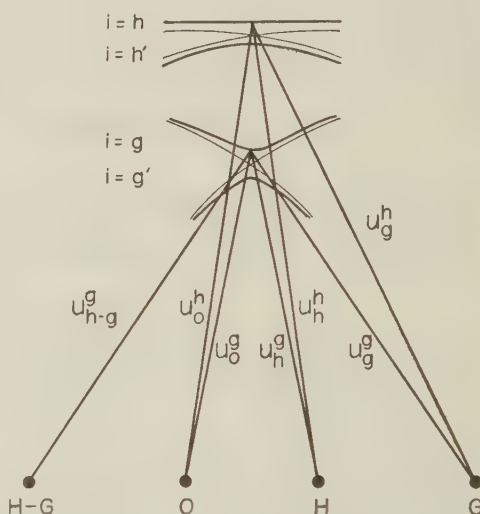


Fig. 1. Relation between amplitudes and wave field.

(1) indicates that the intensity is given by the sum of trigonometric functions of $D/2k$. When we calculate the intensity in fairly large $D/2k$ by the use of power expansion of $D/2k$, the number of terms to be taken into account is determined by the maximum value of $|x^i - x^j|$. However, the higher terms are very complicated, necessitating difficult calculations.

Let us denote as I_h^g , the intensity of h -reflection given by the matrix M which is formed by taking account of reflections corresponding to the reciprocal lattice points from G to $H-G$ (Fig. 1). If the value

$$\frac{I_h^g - I_h^{g-1}}{I_h^{g-1}} \quad (2)$$

is very small compared with unity for all $D/2k$, it is practical not to take into account of G and $H-G$, because this makes favourable the convergence of the power series on ac-

* The term "higher order reflection" indicates the higher order reflection of a non-vanishing reflection, such as 222 or 333 of f.c.c. lattice. This should not be confused with the "high index reflection", e.g. 511 and 420 of f.c.c. lattice for which $h^2 + k^2 + l^2$ is large.

count of the smaller maximum value of $|x^i - x^j|$, and at the same time, we can drop from I_h^g the $\sin^2$ -terms representing small ripples of short periods due to large $|x^i - x^j|$ in the I_h vs $D/2k$ curve.

For small $D/2k$, I_h^g and I_h^{g-1} are given by

$$\left. \begin{aligned} I_h^g &= I_h^{g-1} = \left(\frac{D}{2k} \right)^2 v_h^2 \\ \text{and} \\ I_h^g &= -2 \sum_{i,j} u_h^i u_h^j \left(\frac{D}{4k} \right)^2 (x^i - x^j)^2, \end{aligned} \right\} \quad (3)$$

but they are not equal to each other for large $D/2k$. As it is tedious to compare directly I_h^g with I_h^{g-1} for large $D/2k$, we may use $I_h^{g'}$, namely

$$I_h^{g'} = -2 \sum_{i,j \neq g, g'} u_h^i u_h^j \sin^2 \left[\frac{D}{4k} (x^i - x^j) \right], \quad (4)$$

in place of I_h^g , since $u_h^{g, g'}$ are small for large g so that we can neglect the terms including $u_h^{g, g'}$ in I_h^g . As each value of $x^i - x^j$ in $I_h^{g'}$ is almost equal to the corresponding value in I_h^{g-1} ,* the value

$$\frac{I_h^{g'} - I_h^{g-1}}{I_h^{g-1}} \equiv \frac{\Delta I_h^g}{I_h^{g-1}} \quad (2')$$

may be used instead of (2). This value, however, may be of the same order of magnitude for all range of $D/2k$. For estimation of ΔI_h^g , it is necessary to get the approximate values of the amplitudes of waves of each wave field.

Table I. Values of v_h/β^2 corrected by the temperature factor and used in the numerical calculation.

h	111	222	333	444	555	$\beta = 2\pi/d_{111}$ (Å ⁻¹)
Al	0.214	0.0732	0.0360	0.0183	0.0089	2.690
Au	0.770	0.362	0.190	0.0922	0.0585	0.670

Therefore, we have

$$u_h^g = \phi_0^g \phi_h^g = \frac{1}{2} \left(\frac{v_g + v_{h-g}}{p_g - v_h} \right)^2. \quad (10)$$

Similarly,

$$u_h^{g'} = \phi_0^{g'} \phi_h^{g'} = -\frac{1}{2} \left(\frac{v_g - v_{h-g}}{p_g + v_h} \right)^2. \quad (10')$$

Applying (10) and (10') to the 111-reflections of Al and Au, and introducing the numerical values relating to the potential coefficient v 's

* x^i and u_h^i in I_h^g are not strictly equal to those in I_h^{g-1} ,

One of the fundamental equation of the dynamical theory may be written as

$$(k^2 - k_0^2) \phi_0 + \sum_g v_{-g} \phi_g = 0 \quad (5)$$

and

$$k^2 - k_0^2 = -x + p_g.$$

For systematic interactions, p_g is given by

$$p_g = 2k\rho_g + \rho_g^2 = -g(g-h)\beta^2, \quad (6)$$

where ρ_g is Anregungsfehler and $\beta = 2\pi/d_1$.

For eigen vectors ϕ^g at the Bragg position, we have the following relationships, namely

$$\phi_i^g = \phi_{h-i}^{g'}, \quad \phi_i^{g'} = -\phi_{h-i}^g. \quad (7)$$

Among the components of the normalized ϕ^g , the largest components are approximately given by

$$\phi_g^g = \phi_{h-g}^g = \frac{1}{\sqrt{2}}, \quad (8)$$

and other components may be very small compared with ϕ_g^g and ϕ_{h-g}^g . The eigen value x^g , corresponding to large g , is approximately given by

$$x^g = p_g.$$

Neglecting small terms in (5), we have

$$-p_g \phi_0^g + v_g \phi_g^g + v_{h-g} \phi_{h-g}^g + v_h \phi_h^g = 0, \quad (9)$$

since

$$v_g = v_{-g}.$$

Substituting (7), (8) into (9), we obtain

$$\phi_0^g = \frac{v_g \phi_g^g + v_{h-g} \phi_{h-g}^g}{p_g - v_h} = \frac{1}{\sqrt{2}} \frac{v_g + v_{h-g}}{p_g - v_h}.$$

Table II. Values of the amplitude of 111-reflection wave at the Bragg position, belonging to each wave field.

	u_1^2	$u_1^{2'}$	u_1^3	$u_1^{3'}$
Al	0.0084	-0.0031	0.00016	-0.00002
Au	0.083	-0.055	0.003	-0.0005

shown in Table I, we can obtain the values of u 's shown in Table II, where the subscript 1 stands for (111). These results show that $|u_h^i|$ ($i \neq h, h'$) are very small compared with

$|u_h^{h,h'}|$ ($|u_h^{h,h'}|$ are approximately equal to $1/2$), so that we can use $I_h^{g'}$ instead of I_h^g for large $D/2k$. Even if $|u_h^i|$ ($i \neq h, h'$) are small, however, we cannot say that (2') is small.

As the magnitude of (2') may be of the same order for all $D/2k$, it is sufficient to evaluate (2') for small $D/2k$. Using (3) and (4), we have for small $D/2k$

$$\begin{aligned} \Delta I_h^g = & 4 \sum_{i \neq g, g'} \left[u_h^i u_h^g \left(\frac{D}{4k} \right)^2 (x^i - x^g)^2 \right. \\ & + u_h^i u_h^{g'} \left(\frac{D}{4k} \right)^2 (x^i - x^{g'})^2 \Big] \\ & + 4 u_h^g u_h^{g'} \left(\frac{D}{4k} \right)^2 (x^g - x^{g'})^2. \end{aligned} \quad (11)$$

The important terms in the summation of (11) are those for which $i = h, h'$, and we may assume $u_h^h = -u_h^{h'}$ and $x^h - x^{h'} = 2v_h$ for the first order reflection, therefore, we have

$$\begin{aligned} \Delta I_h^g = & \left(\frac{D}{2k} \right)^2 [u_h^h u_h^g (v_h - p_g)^2 + u_h^{h'} u_h^g (v_h + p_g)^2 \\ & + u_h^h u_h^{g'} (v_h - p_g)^2 + u_h^{h'} u_h^{g'} (v_h + p_g)^2] \end{aligned} \quad (11')$$

instead of (11). Putting (10), (10') into (11'), we obtain

$$\Delta I_h^g = \left(\frac{D}{2k} \right)^2 v_h p_g \left[\left(\frac{v_g - v_h - g}{p_g + v_h} \right)^2 - \left(\frac{v_g + v_h - g}{p_g - v_h} \right)^2 \right].$$

Taking as

$$I_h = \left(\frac{D}{2k} \right)^2 v_h^2,$$

we have

$$\frac{\Delta I_h^g}{I_h} = \frac{p_g}{v_h} \left[\left(\frac{v_g - v_h - g}{p_g + v_h} \right)^2 - \left(\frac{v_g + v_h - g}{p_g - v_h} \right)^2 \right]. \quad (12)$$

In the case of the 111- and 333-reflections of Al and Au, the values of (12) are shown in Table III. Values for the 111-reflection show that we can not neglect the influence of the

222-reflection on the 111-reflection*. If we permit an error of 0.8% for Al, of 4% for Au, we may neglect the contribution of the 333-reflection. This result indicates that the four-wave approximation may be sufficient for calculating the intensities of the 111-reflection for Al and Au. Values for the 333-reflection show that the effect of the 444-reflection can not be neglected, and the six-wave approximation is necessary in this case. However, the two-wave approximation is sufficient for the first order reflection of high index, such as 511-, since the influence of the 10,2,2-reflection on the 511-reflection of Au is about 2% (in this case, $v_{511}/\beta^2 = 0.0267$, $v_{10,2,2}/\beta^2 = 0.0096$ and $\beta = 2\pi/d_{511} = 8.07 \text{ \AA}^{-1}$).

§ 3. Critical Thickness of the First Order Reflection for the Kinematical Theory

As mentioned above, we may get a fairly

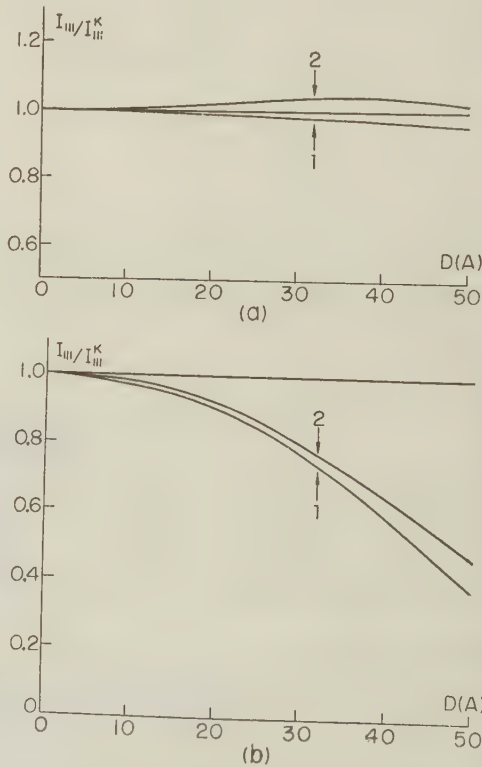


Fig. 2. Intensity ratio to kinematical theory of 111-reflections from (a) Al and (b) Au at Bragg position (in each case, $k=100\text{\AA}^{-1}$). (1) two-wave approximation. (2) expansion of scattering matrix.

* The actual influence of the 222-reflection on the 111-reflection is smaller than that estimated here, as we shall see in the next section (Fig. 2).

Table III.

(a) Values of (12) for the 111-reflection.

	$g=(222)$	$g=(333)$
Al	0.10	0.008
Au	0.15	0.04

(b) Values of (12) for the 333-reflection.

	$g=(444)$	$g=(555)$
Al	0.10	0.008
Au	0.23	0.04

good approximation for first order reflection, when four reciprocal lattice points are taken into account. We can thus calculate the intensity at the Bragg position by the use of the expansion given in I , and compare the result with that given by the two-wave approximation and by the kinematical theory.[†]

For the sake of easy comparison with the intensity of the kinematical theory, we write the intensity formula as

$$I_h = \left(\frac{D}{2k}\right)^2 v_h^2 G\left(v, \frac{D}{2k}\right). \quad (13)$$

For the 111-reflection of Al and Au, we get for Al

$$G = 1 + 0.0505 \left(\frac{D}{2k} \beta^2\right)^2 - 0.0142 \left(\frac{D}{2k} \beta^2\right)^4 + \dots,$$

for Au

$$G = 1 - 0.123 \left(\frac{D}{2k} \beta^2\right)^2 - 0.0459 \left(\frac{D}{2k} \beta^2\right)^4 + \dots.$$

$G(v, D/2k)$ are shown in Fig. 2 for each case.

As we see from Fig. 2, the result above obtained deviates from that due to the two-wave approximation about 7% for Al and 10% for Au at $D=40$ Å. It is noteworthy that the intensity for Al for small $D/2k$ is higher not only than that of the two-wave approximation but than that of the kinematical theory.

§ 4. Feynman Expansion

It is not easy to calculate the intensity of the higher order reflection from relatively thick crystals, because, as mentioned in Section 2, we must consider many reciprocal lattice points. The complicated calculations of matrix can be, however, simplified to some extent by the use of the method of "Feynman expansion".⁷⁾

When the matrix M is expressed as the sum of two matrixes M_0 and M' , we have

$$\exp\left(i \frac{D}{2k} M\right) = \exp(A+B) = \exp A \left[1 + \int_0^1 e^{-sA} B e^{sA} ds + \int_0^1 \int_0^s e^{-sA} B e^{s'A} e^{-s''A} B e^{s''A} ds' ds + \dots \right], \quad (14)$$

where

$$i \frac{D}{2k} M_0 = A, \quad i \frac{D}{2k} M' = B. \quad (15)$$

If we can obtain the normalized eigen vectors $\phi_{(0)}^i$ and eigen values $x_{(0)}^i$ corresponding to M_0 , we can transform the matrix $\exp(sA)$ to diagonal matrix $\exp(sX)$, where X is a diagonal matrix with components $X_{ii} = i(D/2k)x_{(0)}^i$. Using a unitary matrix U with components $U_{gi} = \phi_{g(0)}^i$, we have

$$U^{-1} \exp(sA) U = \exp(sX). \quad (16)$$

Therefore, we can obtain the $h, 0$ component of (14) from (15) and (16) as follows

$$\begin{aligned} \left[\exp\left(i \frac{D}{2k} M\right) \right]_{h0} &= \sum_i \phi_{h(0)}^i \phi_{0(0)}^{i*} \exp\left(i \frac{D}{2k} x_{(0)}^i\right) \\ &+ \sum_{i,j} \sum_{g,l} \phi_{h(0)}^i \phi_{g(0)}^{j*} \phi_{l(0)}^j \phi_{0(0)}^{l*} M'_{gl} \left[\frac{\exp(i(D/2k)x_{(0)}^i)}{x_{(0)}^i - x_{(0)}^j} + \frac{\exp(i(D/2k)x_{(0)}^j)}{x_{(0)}^j - x_{(0)}^i} \right] \\ &+ \sum_{i,j,k} \sum_{g,l,m,n} \phi_{h(0)}^i \phi_{g(0)}^{j*} \phi_{l(0)}^j \phi_{m(0)}^{k*} \phi_{n(0)}^k \phi_{0(0)}^{n*} M'_{gl} M'_{mn} \\ &\times \left[\frac{\exp(i(D/2k)x_{(0)}^i)}{(x_{(0)}^i - x_{(0)}^j)(x_{(0)}^j - x_{(0)}^k)} + \frac{\exp(i(D/2k)x_{(0)}^j)}{(x_{(0)}^j - x_{(0)}^i)(x_{(0)}^i - x_{(0)}^k)} \right. \\ &\left. + \frac{\exp(i(D/2k)x_{(0)}^k)}{(x_{(0)}^k - x_{(0)}^i)(x_{(0)}^i - x_{(0)}^j)} \right] + \dots, \end{aligned} \quad (17)$$

[†] The intensity at the Bragg position for real v_h can also be obtained easily by solving directly the secular equation which is separable in this case. Through this fact, we can easily verify the relations (7).

utilizing the relations

$$\begin{aligned}\exp\left(i\frac{D}{2k}M\right) &= UU^{-1}\exp(A+B)UU^{-1} \\ &= U\exp X\left[1+\int_0^1 e^{-sX}U^{-1}BUe^{sX}ds\right. \\ &\quad \left.+\int_0^1\int_0^s e^{-sX}U^{-1}BUe^{sX}e^{-s'X}U^{-1}BUe^{s'X}ds'ds+\cdots\right]U^{-1}\end{aligned}$$

and

$$[U^{-1}BU]_{ij} = \sum_{g,l} i \frac{D}{2k} \phi_{g(0)}^{i*} M'_{gl} \phi_{l(0)}^j.$$

If, for an example illustrating the usefulness of the above expansion,

$$M_0 = \begin{pmatrix} p_0 & & & & & \\ & \ddots & & & & \\ & & p_h & & & \\ & & & \ddots & & \\ & 0 & & & p_g & \\ & & & & & \ddots \end{pmatrix} \quad \text{and} \quad M' = \begin{pmatrix} 0 & \cdots & v_{0h} & \cdots & v_{0g} & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \ddots \\ v_{h0} & \cdots & 0 & \cdots & v_{hg} & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \ddots \\ v_{g0} & \cdots & v_{gh} & \cdots & 0 & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \ddots \end{pmatrix}$$

we can easily verify that each term in (17) is reduced to (32-I), since $x_{(0)}^g = p_g$ and $\phi_{g(0)}^i = \delta_{ig}$.

In this section, we start from the two-wave approximation for a better approximation. Thus we put

$$M_0 = \begin{pmatrix} p_0 & v_{0h} & & 0 \\ v_{h0} & p_h & & \\ & & \ddots & \\ & 0 & & p_g \\ & & & & \ddots \end{pmatrix} \quad \text{and} \quad M' = \begin{pmatrix} 0 & 0 & \cdots & v_{0g} & \cdots \\ 0 & 0 & \cdots & v_{hg} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ v_{g0} & v_{gh} & \cdots & 0 & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{pmatrix}. \quad (18)$$

If we take into account only the systematic interactions and assume that v 's are real, p_g at exact Bragg position for h -reflection can be expressed by (6). U and X corresponding to (18) are given by

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & & \\ & & \ddots & \\ 0 & & & 1 & \ddots \end{pmatrix} \quad \text{and} \quad X = \begin{pmatrix} v_h & & & \\ & -v_h & & 0 \\ & & \ddots & \\ 0 & & & p_g & \ddots \end{pmatrix}. \quad (19)$$

Substituting (19) into (17), the second term vanishes by the relations $\phi_{h(0)}^i, \phi_{0(0)}^j = 0$ (for $i, j \neq h, 0$) and $M'_{gl} = 0$ (for $g, l = h, 0$). The terms for which $i=j$ in the bracket in the third terms of (17) are given by

$$i \frac{D}{2k} \frac{\exp(i(D/2k)x_{(0)}^i)}{(x_{(0)}^i - x_{(0)}^k)} - \frac{\exp(i(D/2k)x_{(0)}^i)}{(x_{(0)}^i - x_{(0)}^k)^2} + \frac{\exp(i(D/2k)x_{(0)}^k)}{(x_{(0)}^k - x_{(0)}^i)^2}$$

and the terms for which $i \neq j \neq k$ vanish. Therefore, (17) is given by

$$\begin{aligned}
\left[\exp\left(i \frac{D}{2k} M\right) \right]_{h0} &= \frac{1}{2} \left[\exp\left(i \frac{D}{2k} v_h\right) - \exp\left(-i \frac{D}{2k} v_h\right) \right] \\
&+ \frac{1}{4} \sum_g \left[(2v_{h-g}v_g + v_g^2 + v_{h-g}^2) \right. \\
&\times \left\{ i \frac{D}{2k} \frac{\exp(i(D/2k)v_h)}{(g(g-h)\beta^2 + v_h)} - \frac{\exp(i(D/2k)v_h)}{(g(g-h)\beta^2 + v_h)^2} + \frac{\exp(-i(D/2k)g(g-h)\beta^2)}{(g(g-h)\beta^2 + v_h)^2} \right\} \\
&+ (2v_{h-g}v_g - v_g^2 - v_{h-g}^2) \\
&\times \left\{ i \frac{D}{2k} \frac{\exp(-i(D/2k)v_h)}{(g(g-h)\beta^2 - v_h)} - \frac{\exp(-i(D/2k)v_h)}{(g(g-h)\beta^2 - v_h)^2} + \frac{\exp(-i(D/2k)g(g-h)\beta^2)}{(g(g-h)\beta^2 - v_h)^2} \right\} \\
&+ \dots \dots \dots \quad (20)
\end{aligned}$$

The first term of (20) represents the result given by the two-wave approximation for the exact Bragg position, and the second term, the effect of double scattering in which electrons are scattered first from the 0- or h -direction to g -direction ($g \neq h, 0$) and then scattered back to the 0- or h -direction. Higher terms which are not written in (20) represent the effect of multiple scatterings except those between 0- and h -directions the effect of

which is included in the first term.

The intensities of the 333-reflections from Al and Au calculated by the first and second terms in (20) taking account of the reciprocal lattice points from $(\bar{1}11)$ to (444) are shown in Fig. 3.

§ 5. Integrated Intensity

The calculation of the integrated intensity which is applicable to the crystal of a considerable thickness is quite complicated, especially for higher order reflections of a strong reflection. For, the intensity of reflection outside the Bragg position must be calculated, for which the calculation of higher terms is necessary, in the expansion (20-I), and, in the Feynman expansion, the analytical integration with respect to incident direction is tedious. The other difficulty is that the number of reciprocal lattice point to be taken into account for the calculation outside the Bragg position is different from that needed for the Bragg position.

To avoid these difficulties, we content ourselves with the calculation of the integrated intensity based upon (29-I). The results for the integrated intensity of the 111-reflections from Al and Au, taking account of the reflections from $\bar{1}11$ to 222, are as follows:

$$\begin{aligned}
J_{111} &= \frac{2\sqrt{3}}{3} \frac{D}{2k^3} \frac{v_{111}^2}{\theta_0} \left[1 + 3.97 \left(\frac{D}{2k} \right)^2 \right] \quad \text{for Al} \\
&\quad \text{and} \\
J_{111} &= \frac{2\sqrt{3}}{3} \frac{D}{2k^3} \frac{v_{111}^2}{\theta_0} \left[1 - 9.74 \left(\frac{D}{2k} \right)^2 \right] \quad \text{for Au}
\end{aligned} \quad (21)$$

where D and k are expressed in Å and in Å⁻¹, respectively. The values in the bracket of (21) are shown in Fig. 4 by the solid

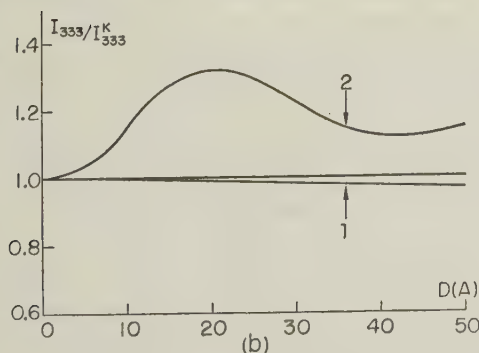
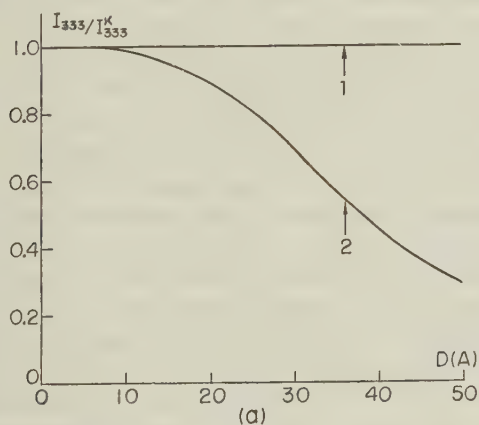


Fig. 3. Intensity ratio to kinematical theory of 333-reflection from (a) Al and (b) Au at Bragg position (in each case, $k=100\text{Å}^{-1}$). (1) two-wave approximation. (2) Feynman expansion of scattering matrix, taking up to second term.

curves. The broken lines are the values which would be expected if the higher terms were exactly taken into account. The lines for the two-wave approximation are the values obtained also by the use of (29-I) eliminated the terms of summation.

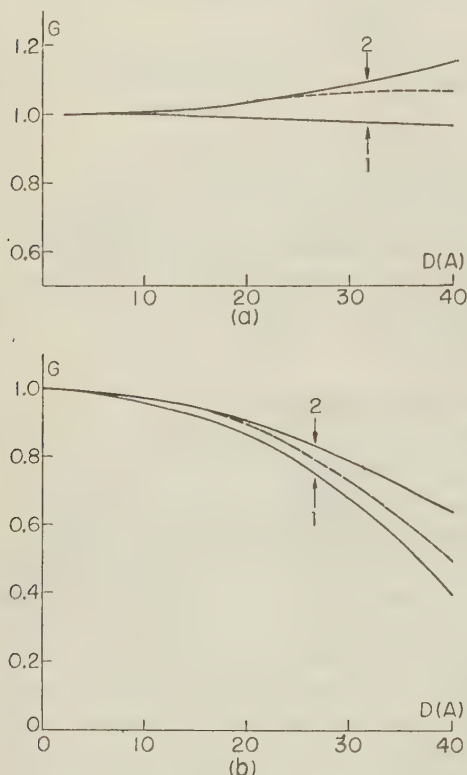


Fig. 4. Integrated intensity ratio to kinematical theory of 111-reflection of (a) Al and (b) Au ($k=100\text{\AA}^{-1}$ and the values are obtain by the quadratic approximation, for each case). (1) two-wave approximation. (2) that given by (21), and the broken lines are the values expected by the correction for higher terms.

§ 6. Discussion

Let us now discuss from the results obtained in the foregoing sections the critical thickness below which the kinematical theory can be safely applied, assuming $k=100\text{\AA}^{-1}$. This critical thickness is different from what is obtained from the two-wave approximation, though the difference is not so large for the first order reflection. If we allow an error of 3% in the intensity, the critical thickness for 111-reflection of Au is 15 Å (Fig. 2). For Al, the intensity is stronger than that given by the kinematical theory for small $D/2k$.

The relative deviation from the kinematical value increases with $D/2k$, reaches the maximum of about 4% at 40 Å, and then decreases to the value -3% at 60 Å. So, 60 Å may be taken as the critical thickness for 111-reflection of Al. If we allow for an error of 10% in the intensity, we have 22 Å and 80 Å for Au and Al, respectively. These values are larger than the corresponding values obtained from the two-wave approximation.

The intensities of 333-reflection for Al and Au deviate considerably from that of the two-wave approximation as seen in Fig. 3. In the case of Al, the ratio of the calculated intensity to that due to the kinematical theory decreases with increasing thickness. Such a tendency seems to be related to the fact that the gap of the dispersion surface for the 333-reflection, $(x^{3'}-x^3)$, is very small compared with $2v_{333}$ as is suggested by the value of the dynamic potential. For Au, the intensity is larger than that of the two-wave approximation. The first maximum arises from the interactions between $u_{31,1'}$ and $u_{34,4'}$ which are of appreciable magnitude. To obtain the higher accuracy, we have to take into account higher terms in expansion, especially for Au, for which v_{111} is large.

Some practical methods as mentioned in Section 1 have been so far developed for obtaining accurate values of v_h , from the experimentally observed intensities of reflections. From above results, however, it is concluded that these methods cannot be free from a few percent error for the first order reflection except for high index reflections, so long as they are based on the two-wave approximation. Further, the deviation from the two-wave approximation is so large for the higher order reflections that the accurate value of v_h may not be expected by these methods, though we did not calculate the integrated intensities of higher order reflection. For the theoretical foundation of the elimination of the dynamic effect in the observed intensity, a more accurate study of the integrated intensity in wide range of thickness and wave length should be desired.

The author would like to thank Prof. S. Takagi for his guidance, and Prof. K. Kohra for his helpful discussions and Prof. T. Matsubara for the suggestion that the Feynman expansion is useful for the calculation

of scattering matrix.

References

- 1) G. Honjo and N. Kitamura: *Acta Cryst.* **10** (1957) 533.
- 2) S. Kuwabara: *J. Phys. Soc. Japan* **14** (1959) 1205.
- 3) S. Nagakura: *Acta Cryst.* **10** (1957) 601; *J. Phys. Soc. Japan* **13** (1958) 1005.
- 4) M. Blackman: *Proc. Roy. Soc. A*, **173** (1939) 68.
- 5) J. A. Hoerni: *Phys. Rev.* **102** (1956) 1534.
- 6) F. Fujimoto: *J. Phys. Soc. Japan* **14** (1959) 1558.
- 7) R. P. Feynman: *Phys. Rev.* **84** (1951) 108.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

The Effects of Deuteron Irradiation on the Nuclear Magnetic Resonance in Teflon*

By Hazime KUSUMOTO**

*Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois, U.S.A.*

(Received August 29, 1959)

F^{19} magnetic resonance was observed on non-irradiated Teflon and irradiated one by deuterons. Irradiation caused considerable increase of line width and second moment above -75°C , where an abrupt narrowing of line width caused by the onset of the segmental motion of the molecules took place for both samples. This result suggests that there might exist in the irradiated Teflon some molecular structures disturbing the molecular motion, e.g., cross-linkings, double bonds, formation of ring etc. and/or increase of crystallinity by irradiation. A broad line component superimposed on a sharp absorption line observed in the original Teflon around -7°C faded out as a result of the irradiation. The energies and entropies of activation were computed from the line width data. The irradiation gave them the effects similar to those of curing in natural rubber.

§ 1. Introduction

Several authors¹⁾⁻⁵⁾ have reported on the investigation of Teflon (polytetrafluoroethylene, P.T.F.E.) by the method of nuclear magnetic resonance (N.M.R.). The features of variations of line widths and second moments have been reported to be somewhat different depending on the samples examined. In some cases^{1), 5)} absorption lines, which consisted of a sharp central peak and a broad weak line in some temperature region, were observed. From line shapes and T_1 measurements by the pro-

gressive saturation method⁵⁾ they concluded that these two components of the absorption line are due to the amorphous phase and crystalline one in the polymer, respectively. However, the others²⁾⁻⁴⁾ did not observe such peculiar line shapes in the temperature region where they might be expected to occur but observed merely bell-shaped resonance lines having long tails and inflection points, which had an abrupt motional narrowing region between about -80°C and room temperature. The features in this temperature region seem likely to depend on the nature of the samples.

Meanwhile it has been reported⁶⁾ that irradiation causes dissociation of Teflon molecules, $(\text{C}_2\text{F}_4)_n$, and that consequently they become small fraction of pieces or powder. The

* Read at the Faculty Meeting on High Polymers of the Physical Society of Japan at Tokyo University of Science on April 1, 1959.

** Now at Hitachi Central Research Laboratory, Kokubunzi, Tokyo, Japan.

mechanism of dissociation is believed principally to be that, in Teflon molecules, the strong C-F bonds are not broken but the rather weak C-C bonds are cut down by irradiation, and, in contrast with the case of polyethylene cross-linked by irradiation⁷⁾, shorter molecules are produced. Such a change of the molecular structures could be detected by the method of N.M.R. on F^{19} nuclei attached directly on the carbon atoms of the molecular chains, since the spectrum is sensitive to the situation of the nuclei observed. Preliminary measurements⁸⁾ were made on these effects at room temperature as reported elsewhere and observation has been carried out down to liquid nitrogen temperature as presented in this article.

§ 2. Experimental Procedures

The resonance was observed with usual autodyne oscillators and permanent magnets. These equipments have been described elsewhere^{9), 10)}.

The sample were furnished very kindly by Professors K. Ono* and H. Abe* of the Institute of Science and Technology, University of Tokyo. The original Teflon was commercial film, 50μ in thickness. This film was irradiated by deuteron beams inside of the cyclotron. The beam current was $2\mu A$. Since it was irradiated in vacuo, no effect of oxidation could be expected at bombardment. To make the effects of irradiation uniform the films were wound around a brass cylinder, which could be rotated from the outside of the beam passage, and were irradiated repeatedly. After the irradiation the sample lost elasticity and became small pieces easily. The other four sheets were irradiated in the same way for 20 sec., 1 min., 3 min., and 10 min., respectively. No examination was made for determining the radiation does and quantity of released gases about these experiments. However, the deuteron beam current and irradiation time in this experiment suggest, in comparison with the case of a similar experiment by the same cyclotron¹¹⁾, that the radiation dose might be of the order of 10^9 rad or more for the powdered sample and of 10^7 – 10^8 rad for the other four specimens.

§ 3. Experimental Results and Discussions

3.1 Line width and line shape

In the first place the line width and shape were observed at room temperature as briefly reported earlier⁸⁾. The original Teflon had very sharp absorption line with long tails. The max. and min. slope line width was about 0.7 gauss. There was observed no remarkable broad component. While, on the irradiated Teflon a simple broad line, ΔH_{msl} , of which was 2.8 gauss, was observed. Changes on the line shape of four samples differing in irradiation time fell between those of the original Teflon and exhaustively irradiated sample. Although the line width change was not so remarkable, it could still be recognized how irradiation changed line shapes. The line width data at $25^\circ C$ are summarized in Table I and some of the observed derivatives of absorption lines are reproduced in Fig. 1 (a), (b), (c) and (d). As can be seen there,

Table I. The line widths and second moments of Teflon and irradiated Teflons at $25^\circ C$.

	Original Teflon	Irradiated Teflon				
		Powdered	20 sec.	1 min.	3 min.	10 min.
ΔH_{msl}	0.7 gauss	2.8	0.77	0.92	1.1	1.3
ΔH_2^2	1.9 gauss ²	3.4	3.0	3.1	3.3	3.0

Note: The data in reference (8) were observed at $32^\circ C$.

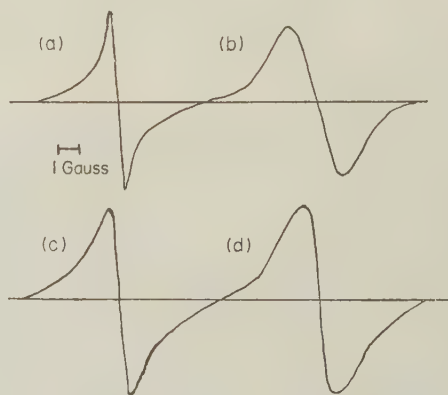


Fig. 1. Derivative curves of various samples of Teflon and irradiated ones at $25^\circ C$.

- (a) Original Teflon
- (b) Teflon irradiated exhaustively
- (c) Teflon irradiated for 1 min.
- (d) Teflon irradiated for 10 min.

* Now at The Institute for Solid State Physics, University of Tokyo,

the sharp central peak of the original sample became broad with increasing irradiation time and line shapes seem to approach that of the exhaustively irradiated sample. Since the narrow line width of the original Teflon at room temperature is due to the segmental motions of the molecules¹⁻⁴, the broadened widths of the irradiated Teflon would suggest that the molecular motions in these compounds might be disturbed much more than those in the non-irradiated one.

To make sure this point of view we observed temperature dependence of the line widths of the original and powdered Teflon in the temperature range from -190°C to 80°C , where line widths of both samples were almost level-off. Since the effects of irradiation for the other samples seemed to be small, we examined only two extreme cases.

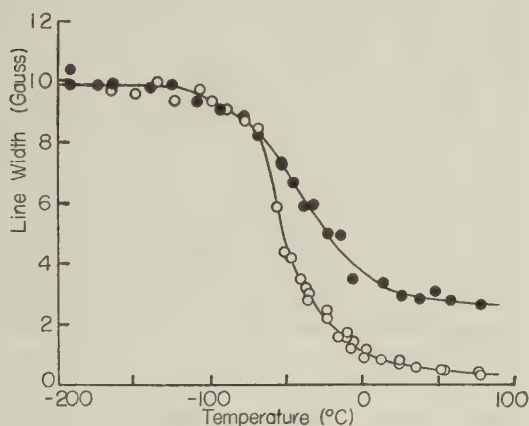


Fig. 2. Line width variation with temperature for the original Teflon (open circles) and the irradiated one (filled circles).

The whole features of variation of the line widths defined as separation of the max. and min. slope of absorption lines and second moments are shown in Fig. 2. Both samples might be in rigid state below -110°C , where line widths were about 9.9 gauss, which is quite consistent with the values reported on Teflon³. There was a gradual narrowing region between -110°C and -75°C for both samples in common. The line width dropped from 9.9 gauss to 8.9 gauss. An abrupt narrowing took place at about -75°C , above which the difference between the original sample and the irradiated one was observed obviously. From -75°C to about 10°C line widths decreased to 3.1 gauss for the irradiated

sample and 0.8 gauss for the original one, respectively. These values still decreased very gradually with increasing temperature and reached to 0.5 gauss for the original Teflon and 2.8 gauss for the irradiated Teflon at 80°C .

The line shapes below -75°C were similar to those reported by other authors¹⁻⁵ and no peculiar structures were observed. A typical line shape below -100°C , where the both samples might be considered in rigid state, is shown in Fig. 3. The line shapes were almost identical for these two samples in this temperature region.

Remarkable line shapes observed were those of the original Teflon in the temperature range between -15°C and 12°C . There existed a sharp line superimposed on a broad line, which

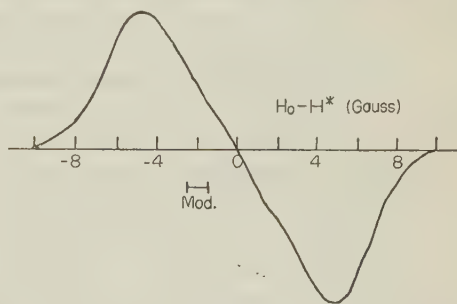


Fig. 3. A typical derivative curve of the original Teflon at -196°C .

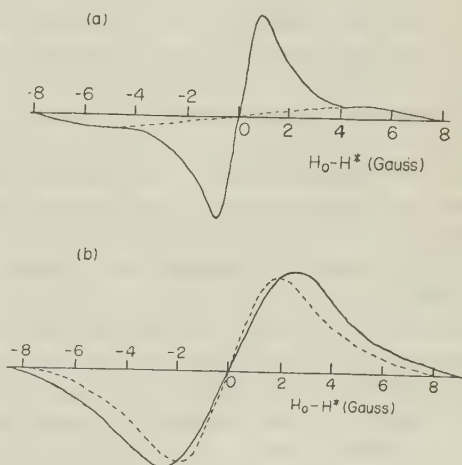


Fig. 4. Derivative curves of the original Teflon and the irradiated one in the transition range.
(a) Original Teflon at -7°C
(b) Irradiated Teflon
Solid curve at -14°C
Dotted curve at -4°C

seemed to have the broad line width as observed in rigid state. Such line shapes were not observed on the irradiated sample, though they were accompanied by long tails. In Fig. 4 typical line shapes somewhat smoothed are shown for both samples. More detailed discussion will be given in the next section in connection with the data of second moments.

General features of motional narrowing in high polymeric system depend upon their mobility. For example, the temperature region of motional narrowing of rubber shifts from the range, $-50 \sim -20^\circ\text{C}$, for raw rubber to the range, $50\text{--}100^\circ\text{C}$, for hard rubber containing 31% of combined sulphur^{(12), (13)}. Meanwhile, in silicone rubber⁽¹⁴⁾, such a temperature region exists between -120°C and -90°C . Furthermore such micro-Brownian motion of the molecules narrows line width up to the order of 0.1 gauss or less. From these features it would be suggested that there might exist some structures which disturb the segmental motion of the molecules in the irradiated Teflon as discussed as follows.

According to Charlesby⁽⁶⁾, the main effect of irradiation has been described such that irradiated Teflon, if irradiation is enough, decomposes to coarse powder. This decomposition is more eminent on block Teflon than on film one. At the same time weight losses and releasing of gases (particularly CF_4) are observed in amount proportional to the surface area and the square of the radiation dose. Charlesby suggested that the decomposition might occur at C-C bonds mainly because C-F bond is stronger than C-C bond⁽¹⁵⁾. On the other hand, several authors have reported paramagnetic resonance on the unpaired electrons of Teflons irradiated by X-rays^{(16), (17)} or deuterons⁽¹¹⁾, which were believed to be produced at broken C-C bonds. The results and conclusions are summarized as follows; (1)⁽¹¹⁾ number of unpaired electrons produced are proportional to irradiation dose in the range of irradiation dose, about $10^7\text{--}10^8$ rad but for the increased dose, density of unpaired electrons reached to the saturated value of 1.4×10^{19} per c.c.; (2)⁽¹¹⁾ the free radicals produced were so stable that no change of line shapes and intensity of resonance absorption was observed after aging in the air for two months; (3)⁽¹⁶⁾ there was some possibility that broken chains might form a loop of some type; (4)⁽²⁰⁾

the primary effect of irradiation in vacuum is to remove an F atom without breaking the C-C chain. Furthermore the fact that CF_4 gas was released would suggest existence of free radicals of type $\dot{\text{C}}\text{F}-\text{CF}_2-$. These free radicals have possibility to make structures as follows, $-\text{CF}=\text{CF}_2-$, $-\text{CF}-\text{CF}_2-$,



etc. These structure have not been certified yet. From the experimental results (1), it might be considered that, if radiation dose exceeds 10^8 rad, excessive population of free radicals would produce certain type of recombination of the free radicals as suggested above. If the free radicals distribute uniformly over the molecules, the saturated density of unpaired electrons gives distribution density of a free radical per about 900 monomers of Teflon. Therefore, if radiation dose is quite enough the supposed structure would reach considerable quantity. Unfortunately, since the radiation dose and released gases were not examined for this experiment, quantity of cross-linking, double bonds and loops could not be estimated*.

We must also consider the effect of crystallinity to line width broadening. It could not be negligible in some cases^{(12), (18), (19)}. It was reported that amorphous phase of isotactic polypropylene⁽¹⁹⁾ has line widths about four times those of atactic (amorphous) polypropylene around their transition temperature regions. Natural rubber quenched to low temperature after annealing⁽¹²⁾ showed narrower line widths than those untreated. Crystallization due to elongation also had effect to broaden line widths⁽¹⁸⁾. Nishioka confirmed⁽²²⁾ about γ -irradiated Teflon by means of X-ray and density measurements, though rather qualitatively, that its crystallinity had tendency to increase after high degree of irradiation, more than of 10^4 r. Line width and shape change by irradiation, then, could occur also in the case of irradiated Teflon by increasing of crystallinity.

* In the case of natural rubber there are produced 10 to 40 cross-linkings per a primary molecule in usual process of vulcanization. Then cross-linkage might be in the order of 10^{-2} per a monomer. The order of this cross-linkage made large effects on the N.M.R. spectrum in natural rubber⁽¹²⁾.
⁽¹³⁾. Refer to: P. J. Flory: *Principles of Polymer Chemistry* (Cornell University Press, 1953) 459.

Another effect expected is oxidation after irradiation¹⁶⁾. Line width and shape of both N.M.R. and E.P.R.¹¹⁾ did not show any change even several months after irradiation. Then, such effects would occur just after irradiation. The effects has been studied by Gordy and his co-workers and they seem likely to be not so important to line width broadening in N.M.R.

3.2 Second moments

Extensive efforts²⁾⁻⁴⁾ have been made to compare experimental second moments with theoretical ones for the structural model of Teflon in rigid state. The exact theoretical values would be very hard to obtain for this polymer because of lack of knowledge on its complicated structure of inter- and intra-molecular arrangement and of coexistence of amorphous and crystalline phase in rigid state. The calculated results, however, suggested that the molecules might be in rigid state below -100°C giving second moment values about 11 gauss², which was in good agreement with the observed values. Our results also fell near to this value for both samples and would suggest that the irradiation may not give change to the principal arrangement of the monomer of molecule seriously. The whole features of second moments variation are shown in Fig. 5.

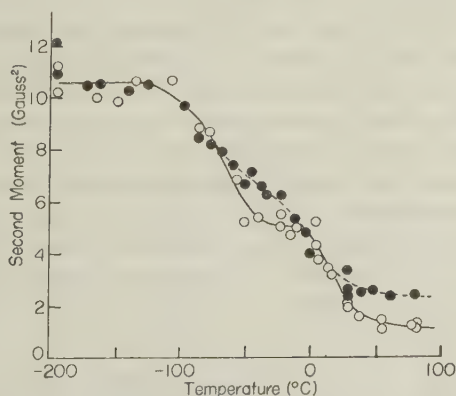


Fig. 5. Second moments variation with temperatures for the original Teflon (open circles) and the irradiated one (filled circles).

Second moments had constant value, about 10.6 gauss², for both samples below -100°C . The original sample showed a behavior similar to that reported by Smith²⁾. The values of second moment decreased from the value of 10.5 gauss² at -100°C to 5.5 gauss² at 40°C .

These values are consistent with Smith's data. There was observed almost constant second moment, about 5 gauss², in the temperature range from -40°C to -7°C . A complex line shape was observed in and above this region. The second motional narrowing followed and finished with the final value of 1 gauss² above 80°C . On the other hand, almost smooth variation of second moment was obtained for the irradiated Teflon, though a slight hump seemed to exist on the curve for the corresponding temperature range. Above 50°C , second moment attains the level-off value, 2.2 gauss². As a whole, the irradiation gave pronounced effects to the temperature dependence of second moment. These are summarized as follows:

(1) Increasing of the value of second moment above the temperature where motional narrowing takes place.

(2) Changing of the hump on the second moment curve of the original Teflon.

About the complex line shape observed for the original Teflon, the method of Wilson-Pake¹⁾ gave the degree of crystallinity of $60 \pm 5\%$, which is lower than the value reported by them. Also contributions from the amorphous and crystalline phase to second moment can be estimated from these absorption lines with appropriate weighting. The observed second moment may be given by the following relation,

$$(\Delta H_2^2)_{\text{obs.}} = (1-x)(\Delta H_2^2)_{\text{sh.}} + x(\Delta H_2^2)_{\text{br.}} \quad (1)$$

where x is degree of crystallinity, $(\Delta H_2^2)_{\text{sh.}}$ and $(\Delta H_2^2)_{\text{br.}}$ stand for contribution of second moments from the sharp and broad lines, respectively. If the broad line corresponds to absorption by the crystalline part of the molecules, which would be almost in rigid state, $(\Delta H_2^2)_{\text{br.}}$ may be in the order of magnitude of second moment observed below -110°C . From the experimental value at -17°C , x was obtained as about 0.6. The contribution, $x(\Delta H_2^2)_{\text{br.}}$, then becomes about 6 gauss², which is not reasonably compared with $(\Delta H_2^2)_{\text{obs.}}$, 4.9 gauss² at that temperature. Actually the second moment of the broad line can be computed on the decomposed component, which gives $(\Delta H_2^2)_{\text{br.}}$ about 7.2 gauss². At other temperatures the contribution was computed as 7~8 gauss². Differences were caused by weak intensity of the components. These values are lower than 10.5 gauss² in rigid

state. Since the value of second moment obtained from derivative curves deviate considerably depending on the cut off point of the tail, rather arbitrary decomposition of derivative curves near inflection points gives only rough estimation of the second moments of the sharp components. The estimated values of $(\Delta H_2^2)_{sh.}$ were 1~2 gauss². The relation (1) also does not give exact values. However, the difference between $(\Delta H_2^2)_{sh.}$ and $(\Delta H_2^2)_{br.}$ was distinct and it may be suggested that in this temperature range about 60% of the molecules belongs to the crystalline phase but may not be in rigid state. Smith²⁾ did not observe clear broad components and explained the hump of the second moment curve more quantitatively using the method gear model proposed by Andrew²¹⁾ for explaining the behavior of hydrocarbons. However, since in our measurements there were observed complex line shapes, which could be decomposed into two parts, it would seem inadequate to apply this model to explain the whole behavior of the molecules. As long as the exact intra- and inter-molecular second moments could not be calculated exactly, we may not be able to get exact explanation for these behaviors. In conclusion, our data of second moments might suggest existence of amorphous parts in motion and crystalline parts probably being in some kind of motion, for example, torsional oscillation around their molecular axes.

On the other hand the irradiated sample showed no complex line shape over the whole temperature range. There still remained slight hump on the curve of temperature variation of second moment. This result led us to suppose that there still exists the crystalline phase in the irradiated sample.

If irradiation does not increase the degree of crystallinity, and if we assume that the second moment of crystalline phase is 7.6~10.6 gauss² and the degree of crystallinity is 60~40%, using the observed $(\Delta H_2^2)_{obs.}$ the relation (1) gives $(\Delta H_2^2)_{sh.}$ as about 4~5 gauss². Therefore it is reasonably suggested that the increasing of $(\Delta H_2^2)_{obs.}$ may be mainly due to broadening of the amorphous component. This increasing of the second moment of amorphous phase could be caused by cross-linking and other structure changes as mentioned before.

If the crystalline phase could be increased

by irradiation²²⁾, the relation (1) allows maximum value of x as 0.7 for the obtained $(\Delta H_2^2)_{obs.}$, 6 gauss², at -12°C assuming that $(\Delta H_2^2)_{sh.}$ is not less than 2 gauss². Therefore, if degradation of the molecules would permit more vigorous motion of the segment in amorphous phase, x could have larger values up to about 0.8. However, since crystallization could disturb such motions in the amorphous region, these assumptions may be unreasonable.

These discrepancies make very difficult to get true mechanism of line width broadening. However, from the second moment data the most likely conclusion obtained might be that the amorphous phase cross-linked causes the increasing of second moment above the transition temperature region.

§ 4. Activation Energy and Entropy

For the relaxation mechanism represented by a single correlation time τ_c ²³⁾, variation of line widths and second moments make possible estimation of activation energies. Though such a single correlation time could not express the complicated micro-Brownian motion of high polymeric systems exactly¹²⁾, treatment might be done for the present purposes as a first approximation.

In the previous section we considered that the second moment of the original Teflon and irradiated one would contain contributions from the two phases. Unfortunately we could not decompose some absorption lines into two phases and discussion could not be made on each phases. Therefore computation of activation energies and entropies was considered about the amorphous phase only, assuming that the obtained line widths represent those of the amorphous phase and applying the B.P.P.'s theory²³⁾,

$$(\Delta H)^2 = M^2 + (R^2 - M^2) \cdot (2/\pi) \cdot \tan^{-1}(\delta\nu/\nu_c) \quad (2)$$

where ΔH is line width in gauss, R and M are line widths in rigid state and in motion, respectively. ν_c is a correlation frequency defined as $\tau_c = (2\pi\nu_c)^{-1}$ and $\delta\nu$ stands for line width in frequency scale having relation $\Delta H = (2\pi/\gamma)\delta\nu$.

According to the theory of rate process²⁴⁾, a unit of motion in molecules might transfer from a stable position to another one with some possibility through unstable activated state. The possibility is given by

$$K' = (kT/h) \exp(-\Delta F^*/RT) \quad (3)$$

We may rewrite this formula for our system

$$\begin{aligned} K'/2\pi &= 1/2\pi\tau_c = \nu_c \\ &= (kT/2\pi h) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT), \end{aligned} \quad (3')$$

Eqs. (2) and (3') give activation energies and entropies for the line width transition region. The results are shown in Table II.

Table II. Activation energies and entropies at -40°C .

Sample	ΔH^* (Kcal/mol)	ΔS^* (e.u.)
Original Teflon	2.8	-19.7
Irradiated Teflon	2.5	-22.7

Note: Temperature dependence of ΔH^* and ΔS^* were about ± 0.1 Kcal/mol and ± 0.2 e.u., respectively, for both samples in the transition temperature range.

Simplified treatment on correlation time can not, with these values, clarify the complicated relaxation mechanism of high polymeric system²⁵⁾.

However, it seems to be significant to compare ΔH^* and ΔS^* computed from line width data on various high polymers. Table II shows that ΔH^* and ΔS^* have tendency to decrease with increasing of irradiation. This fact is interesting to compare the similar results on cured rubber¹³⁾. 2% of combined sulphur was found to decrease the activation entropy from 24 e.u. for uncured rubber to 20 e.u. and 20% of combined sulphur reduced ΔS^* up to 0. Such structures as cross-linking reduce cooperative movement of the segments and result in decreasing of a activation energies and entropies. The obtained large negative value of entropy, -19.7 and -22.7 e.u., are significant. Such negative values of entropies would be expected for another "plastic" polymers, meanwhile, large positive value of entropy would represent segmental motions of "rubberlike" polymers which would be very "cooperative" compared with "plastic" polymers. This tendency would be vice versa. Swelled polyisobutylene²⁶⁾ also showed this tendency. That is, swelling increased activation energies from 10.2 Kcal/mol to 12.6 Kcal/mol and activation entropies from 6 e.u. to 22.3 e.u. Swelling makes the movements of the segments easier and they would become

more cooperative. That is, the movement of a specified segment could reach to another far away from it. The structures like cross-linking, double bonds, loops etc. probably would stop transmission of such movement.

§ 5. Conclusions

Irradiation on Teflon makes the long molecules shorter and consequently its melt viscosity decreases with increasing of irradiation dose²⁷⁾. It was reported that γ -irradiation, about 3×10^4 r, made 1~2 degradation per a molecule of Teflon²⁷⁾. Furthermore, Nishio²²⁾ observed the density of irradiated Teflon increased proportionally to logarithm of dose of more than 10^3 r and he, by means of X-ray measurements, confirmed qualitatively increasing of crystallinity of the irradiated Teflon. However, in our experiments, it was shown that "structures" disturbing molecular motions gave larger effects on the N.M.R. spectra than the degradation. Some comments were made about the questions that the broadened line might be "narrowed" broad components produced as a result of degradation. However, these do not seem to be reasonable, considering that the narrow sharp line disappeared at all above the motional narrowing temperature. If the broad components based on the crystalline parts were narrowed by degradation, there should be observed two superimposed lines above the transition region of the irradiated Teflon.

The phenomena presented here seem to be very complicated to describe exactly. Infrared spectroscopy and T_1 measurements on Teflon irradiated under limited conditions would be desired for more precise conclusion.

However, it may be concluded that in fact the degradation should occur by irradiation but some kinds of net work produced at the same time and increased crystallinity have more prominent effect on the N.M.R. spectrum. Because the second moments in rigid state are almost the same for the two samples, the density of such structures may not be so high, but have the effects so much as cross-linkages in weakly cured rubber.

Acknowledgement

The author is indebted to Prof. H. S. Gutowsky under whose support this work was carried out. And his sincere thanks are ex-

pressed to Professors E. Abe and K. Ono for their helps about the samples and to Dr. Nishioka of Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corp. for his invaluable comments on our results.

References

- 1) C. W. Willson, III and G. E. Pake: J. Polymer Sci. **10** (1954) 503.
- 2) J. A. S. Smith: Discuss. Faraday Soc. No. 19 (1955) 207, 251.
- 3) A. Nishioka, H. Komatsu and Y. Kakiuchi: J. Phys. Soc. Japan **12** (1957) 283.
- 4) W. P. Slichter: J. Polymer Sci. **24** (1957) 173.
- 5) C. W. Willson, III and G. E. Pake: J. Chem. Phys. **27** (1957) 115.
- 6) A. Charlesby: Nucleonics **12** No. 6 (1954) 18.
- 7) K. H. Sun: Modern Plastics **32** (1954) 141.
- 8) H. Kusumoto: J. Phys. Soc. Japan **12** (1957) 826.
- 9) H. Kusumoto: J. Chem. Phys. **24** (1956) 913.
- 10) H. S. Gutowsky, L. H. Meyer and R. E. McClue: R. S. I. **24** (1953) 644.
- 11) E. Abe: Kobunsi **6** (1957) 457 (in Japanese).
- 12) H. Kusumoto: J. Phys. Soc. Japan **11** (1957) 534. H. S. Gutowsky, et al.: J. Chem. Phys. **27** (1957) 534.
- 13) H. Kusumoto: (to be published).
- 14) H. Kusumoto, H. S. Gutowsky and I. J. Lawrenson: (to be published).
- 15) L. Pauling: *Nature of the Chemical Bond* (Cornel Univ. Press, 1948) 53.
- 16) W. B. Ard, H. Shields and W. Gordy: J. Chem. Phys. **23** (1955) 1728.
- 17) E. E. Schneider: J. Chem. Phys. **23** (1955) 978; Discuss. Faraday Soc. No. 19 (1955) 183.
- 18) K. Oshima and H. Kusumoto: J. Chem. Phys. **24** (1956) 913.
- 19) W. P. Slichter and E. R. Mandell: J. Appl. Phys. **29** (1958) 1438.
- 20) H. N. Rexroad and W. Gordy: J. Chem. Phys. **36** (1959) 399.
- 21) E. R. Andrew: J. Chem. Phys. **18** (1950) 607.
- 22) A. Nishioka, et al.: J. Polymer Sci. **28** (1958) 617.
- 23) N. Bloemberger, E. M. Purcell and R. V. Pound: Phys. Rev. **73** (1948) 679.
- 24) S. Glasston, K. J. Laidler and H. Eyring: *Theory of Rate Process* (McGraw-Hill, New York, 1941).
- 25) A. W. Nolle and J. J. Billings: J. Chem. Phys. **30** (1959) 84.
- 26) J. G. Powles: Proc. Phys. Soc. London **B**, **69** (1956) 84.
- 27) A. Nishioka: Kobunsi Kagaku, **16** (1959) 337 (in Japanese).

On the Intramolecular Light Scattering of the Non-Gaussian Chain

By Akira MIYAKE

Department of Physics, Faculty of Liberal Arts and Science, Shizuoka University

(Received November 28, 1959)

The intramolecular light scattering function $P(\theta)$ of the non-Gaussian chain is investigated. For small values of $s = (4\pi/\lambda) \sin(\theta/2)$, where λ is the wavelength of light in the solution, θ , the scattering angle, $1/P(\theta)$ is given by $1 + (s^2/3)\langle r_G^2 \rangle$, and $\langle r_G^2 \rangle$ the mean square radius of gyration from the center of mass can be calculated according to various theories. For sufficiently large values of s , $1/P(\theta)$ is expanded in terms of $1/s^2$ so as to obtain the asymptotic behavior of $1/P(\theta)$ vs. $\sin^2(\theta/2)$ plot. Excluded volume and swelling effects on $1/P(\theta)$ are discussed in a general way. The asymptotic behavior for large s of the experimental results by Cantow-Schulz is analyzed according to the theory.

§ 1. Introduction

As well known, the light scattering in the high polymer solution is a convenient and keen tool to investigate the molecular weight and the size of the solute polymer. The theory of light scattering in a very dilute and monodisperse polymer solution gives^{1), 2)}

$$\lim_{c \rightarrow 0} Kc/I(\theta) = 1/MP(\theta), \quad (1)$$

where c and M are the weight concentration and the molecular weight of the polymer, K is the material constant including the factor $1 + \cos^2 \theta$ depending on the scattering angle θ (in the case of the natural incident light), $I(\theta)$ the intensity of excess scattering, $P(\theta)$ the intramolecular scattering function given by

$$P(\theta) = \frac{2}{N^2} \sum_{i=1}^N \sum_{j>i}^N \int_0^\infty \frac{\sin sr}{sr} W_{ij}(r) 4\pi r^2 dr, \quad (2)$$

where N is the number of segments per molecule, $W_{ij}(r)$ the probability density of finding the j th segment at a position distant by r from the i th segment,

§ 2. Initial Behavior of $1/P(\theta)$

When s is suitably small, we can expand the factor $\sin sr$ appearing in the integrand of Eq. (2) and obtain

$$\frac{1}{P(\theta)} = \left\{ \frac{2}{N^2} \sum_{i<j} \sum \left(1 - \frac{s^2}{6} \langle r_{ij}^2 \rangle \pm \dots \right) \right\}^{-1} = 1 + \frac{s^2}{3} \langle r_G^2 \rangle + \dots, \quad (5)$$

where

$$\langle r_{ij}^2 \rangle = \int_0^\infty r^2 W_{ij}(r) 4\pi r^2 dr \quad (6)$$

is the mean square distance between the i th and the j th segments, and

$$\int_0^\infty W_{ij}(r) 4\pi r^2 dr = 1,$$

and

$$s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}, \quad (3)$$

λ is the wavelength of light in the solution.

For the Gaussian chain, we have^{1), 2)}

$$P(\theta) = \frac{2}{u^2} (e^{-u} - 1 + u), \quad u = \frac{N}{6} s^2 b^2, \quad (4)$$

where b is the segment length.

In most polymer solutions, however, the deviation from Eq. (4) is caused by the excluded volume effect due to the interaction of chain segments themselves and the swelling effect due to the interaction between chain segments and solvent molecules, both of which are central subjects in the present-day theory of polymer solution.³⁾

The purpose of the present study is to examine the influence of non-Gaussian character of the polymer chain on the light scattering, and especially to clarify the asymptotic behavior of $1/P(\theta)$ for large values of s .

$$\langle r_G^2 \rangle = \frac{1}{N^2} \sum_{i < j} \sum \langle r_{ij}^2 \rangle \quad (7)$$

is the mean square radius of gyration from the center of mass in the chain. Wall *et al.* have assumed⁴⁾

$$\langle r_{ij}^2 \rangle = b^2 N^{1+\varepsilon} (|i-j|/N)^{1+\nu}, \quad \varepsilon \geq \nu \quad (6a)$$

substitution of which into Eq. (7) gives (Appendix I)

$$\langle r_G^2 \rangle = \frac{b^2 N^{1+\varepsilon}}{(2+\nu)(3+\nu)}, \quad (7a)$$

If $\varepsilon = \nu$, then Eq. (7a) is reduced to one already obtained by Peterlin⁵⁾ and Mizutani.⁶⁾ And if $\varepsilon = \nu = 0$, then this is no other than that of the Gaussian chain²⁾

$$\langle r_G^2 \rangle = \frac{b^2 N}{6}. \quad (7b)$$

It is worthy of remarking that Eq. (6a) has been used by Wall *et al.*⁴⁾ to calculate $1/P(\theta)$ numerically by means of high speed digital computer, and by Ptitzyn⁷⁾ to obtain $1/P(\theta)$ analytically in terms of the incomplete Gamma function.

On the other hand, after the newest theories given by Fixman⁸⁾ and Yamakawa-Kurata⁹⁾ we have

$$\langle r_G^2 \rangle = \frac{b^2 N}{6} (1 + 1.276z - 2.077z^2 + \dots), \quad (7c)$$

provided the parameter $z \propto N^{1/2}(1 - \Theta/T)$ is small, where Θ is the Flory temperature of the solution.

Thus, the initial slope of $1/P(\theta)$ *vs.* s^2 plot experimentally obtained may bring about some information on $\langle r_G^2 \rangle$, which is dependent on the non-Gaussian character of the chain.

§ 3. Asymptotic Behavior of $1/P(\theta)$

If we assume the Gaussian distribution for $W_{ij}(r)$

$$W_{ij}(r) = (3/2\pi \langle r_{ij}^2 \rangle)^{3/2} \exp(-3r^2/2 \langle r_{ij}^2 \rangle), \quad (8)$$

despite which $\langle r_{ij}^2 \rangle$ is given by Eq. (6a), then we have

$$P(\theta) = \frac{2}{N^2} \sum_{i < j} \sum \exp\left(-\frac{s^2}{6} \langle r_{ij}^2 \rangle\right), \quad (9)$$

so that for sufficiently large s we obtain (Appendix II)

$$\frac{1}{P(\theta)} \simeq \frac{1+\nu}{2\Gamma(1/1+\nu)} \left\{ \frac{\Gamma(2/1+\nu)}{\Gamma(1/1+\nu)} + \left(\frac{s^2 b^2}{6}\right)^{1/1+\nu} N^{(1+\varepsilon)/1+\nu} \right\}, \quad (10)$$

which is reduced to that of the Gaussian chain, when $\varepsilon = \nu = 0$:²⁾

$$\frac{1}{P(\theta)} \simeq \frac{1}{2}(1+u). \quad (10a)$$

On the other hand, as the theory by Yamakawa-Kurata gives⁹⁾

$$W_{ij}(r) = W_{ij}^0(r) + W_{ij}^1(r) + \dots, \quad (11)$$

$$W_{ij}^0(r) = (3/2\pi b^2 |i-j|)^{3/2} \exp(-3r^2/2b^2 |i-j|), \quad (12)$$

$$W_{ij}^1(r) = \frac{z}{N^{1/2}} \sum_{k < l} (l-k)^{-3/2} \left\{ 1 - (3/2\pi b^2 \nu_{ij})^{3/2} \exp(-3r^2/2b^2 \nu_{ij}) \right\},$$

$$\nu_{ij} = \left\{ \begin{array}{ll} j-i & \text{if } 0 \leq k < l \leq i \text{ or } j < k < l \leq N, \\ (j-i)-(l-k) & \text{if } i < k < l \leq j, \\ (j-i) - \frac{(l-i)^2}{(l-k)} & \text{if } 0 \leq k \leq i < l \leq j, \\ (j-i) - \frac{(j-k)^2}{(l-k)} & \text{if } i < k \leq j < l \leq N, \\ (j-i) - \frac{(j-i)^2}{(l-k)} & \text{if } 0 \leq k \leq i < j < l \leq N, \end{array} \right\} \quad (12a)$$

so for sufficiently large s a tedious calculation of Eq. (2) leads to (Appendix III)

$$\frac{1}{P(\theta)} \simeq \frac{1}{2} \{ (1 + 18.284zN^{1/2} + \dots) + u(1 + 2.612zN^{1/2} + \dots) \}. \quad (10b)$$

§ 4. Excluded Volume and Swelling Effect

Unfortunately, the validity of Eq. (10b) is limited to small values of z , *i. e.* near the Flory temperature, but the deviation of $W(r)$:

$$W(r) = \frac{2}{N^2} \sum_{i < j} W_{ij}(r) = W_0(r) + W_1(r) \quad (11a)$$

from $W_0(r)$: (Appendix IV)

$$W_0(r) = \frac{2}{N^2} \sum_{i < j} W_{ij}^0(r) \simeq \frac{5.22}{N} \left(\frac{3}{2\pi b^2} \right)^{3/2} \left\{ 1 - 0.513 \left(\frac{3r^2}{2b^2} \right) + 0.216 \left(\frac{3r^2}{2b^2} \right)^2 \mp \dots \right\}$$

for $r \ll b$,

$$\simeq 2 \left(\frac{3}{2\pi N b^2} \right)^{3/2} \left(\frac{2N b^2}{3r^2} \right)^2 \exp \left(-\frac{3r^2}{2N b^2} \right) \left\{ 1 - 3 \left(\frac{2N b^2}{3r^2} \right) + \frac{45}{4} \left(\frac{2N b^2}{3r^2} \right)^2 \pm \dots \right\}$$

for $r \gg N^{1/2} b$, (13a)

for arbitrary values of z , is not yet clearly known.¹⁰⁾ If we may assume this to be expressed in terms of the Laplace transform:

$$W_1(r) = \int_0^\infty G(x) e^{-rx} dx, \quad (14)$$

where the normalizing condition requires

$$\int_0^\infty W_1(r) 4\pi r^2 dr = 0 = 8\pi \int_0^\infty \frac{G(x)}{x^3} dx. \quad (15)$$

We can find

$$\langle r^2 \rangle = \frac{1}{2} \int_0^\infty r^2 W(r) 4\pi r^2 dr = \frac{N b^2}{6} + 48\pi \int_0^\infty \frac{G(x)}{x^5} dx \quad (16)$$

and for large values of s (Appendix V)

$$\frac{1}{P(\theta)} \simeq \frac{1}{2} \left[\left\{ 1 + \frac{\pi}{9} (N b^2)^2 W_1'(0) \right\} + u \right]. \quad (17)$$

Of course, $G(x)$ must depend on N , so the deviation of Eq. (16) from Eq. (7b) can be expected, similarly to Eq. (7a).

Now suppose tentatively

$$W_1(r) = -\{A + W_0(0)\} \exp\{-B(1+C)r\} + A \exp(-Br), \quad (14a)$$

where

$$-W_1(0) = W_0(0) = \frac{5.22}{N} \left(\frac{3}{2\pi b^2} \right)^{3/2} \quad (13b)$$

due to the volume exclusion. The condition (15) requires

$$A = \frac{W_0(0)}{C(3+3C+C^2)}, \quad (15a)$$

and the maximum value

$$W_1(r_1) = \frac{W_0(0)}{(1+C)^{1+(4/C)}(3+3C+C^2)} \quad (18)$$

appears at

$$r_1 = \frac{4}{BC} \log(1+C). \quad (18a)$$

In Fig. 1, $W_0(r)$ and $W_1(r)$ are illustrated.

Then Eq. (16) gives

$$\langle r^2 \rangle = \frac{Nb^2}{6} + \frac{W_0(0)}{B^5} \frac{(2+C)}{(3+3C+C^2)(1+C)^2} \quad (16a)$$

and $W_1'(0)$ appearing in Eq. (17) is equal to

$$W_1'(0) = \frac{4+6C+4C^2+C^3}{3+3C+C^2} W_0(0)B. \quad (19)$$

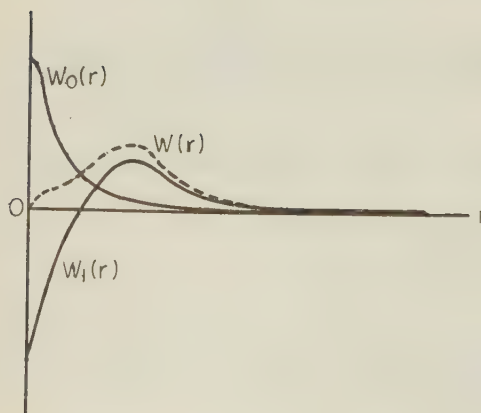


Fig. 1. Schematic graph of $W_0(r)$ and $W_1(r)$.

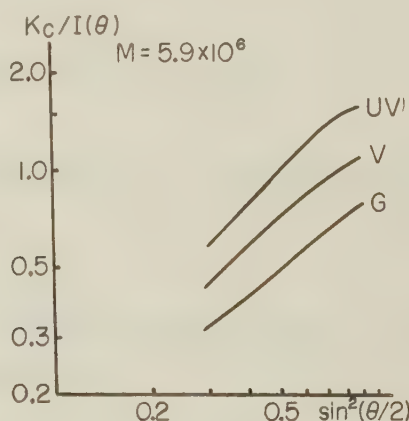


Fig. 2. Log-log plot of $Kc/I(\theta)$ vs. $\sin^2(\theta/2)$ for the sample of $M = 5.9 \times 10^6$. (G): $\lambda = 3996 \text{ \AA}$, (V): $\lambda = 3187 \text{ \AA}$ and (UV): $\lambda = 2664 \text{ \AA}$.

Thus, the initial slope and the asymptotic intercept of $1/P(\theta)$ vs. $\sin^2(\theta/2)$ plot are to present considerable knowledge of the excluded volume and swelling effect, *i. e.* to determine parameters B and C . Or a more detailed theory on statistics of the non-Gaussian chain will be able to predict more about $W_1(r)$.

§ 5. Comparison with the Experimental Result

Till now, experimental difficulties and inaccuracies of the results make a precise compari-

son between the present theory and the experiments very hard. Nevertheless, Cantow-Schulz¹¹⁾ measured the light scattering of well-fractionated samples of polymethyl methacrylate in acetone solution and found in such an initial scattering region, as discussed in § 2, the root mean square end-to-end distance R of the polymer with the molecular weight M equal to

$$R=0.303M^{0.58} \text{ \AA}, \quad \text{for } 3 \times 10^5 < M < 8 \times 10^6, \tag{20}$$

based on the Gaussian chain.

But in the case of non-Gaussian chain these experimental results should give $\langle r_G^2 \rangle$ instead of R as

$$\langle r_G^2 \rangle = 0.0153M^{1.16} \text{ \AA}^2, \tag{21}$$

which is deviating from Eq. (7b).

Unfortunately measured values of $Kc/I(\theta)$ are unsuitable to determine ν accurately by means of Eq. (10) in the asymptotic scattering region, as shown in Fig. 2, where $Kc/I(\theta)$ vs. $\sin^2(\theta/2)$ for the sample of $M=5.9 \times 10^6$ is plotted in log-log scale.

So we must be content to assume

$$\varepsilon = \nu = 0.16 \tag{22}$$

and

$$b^2/m^{1+\varepsilon} = 0.104 \text{ \AA}^2, \tag{23}$$

where m is the molar weight per segment.

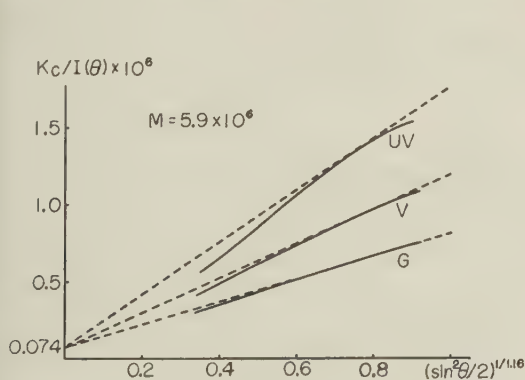


Fig. 3a. $Kc/I(\theta)$ vs. $(\sin^2 \theta/2)^{1/1.16}$ for $M=5.9 \times 10^6$.

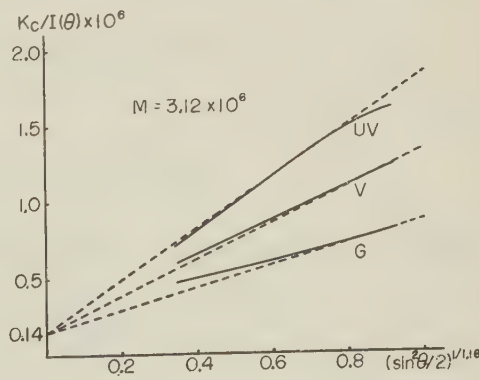


Fig. 3b. $Kc/I(\theta)$ vs. $(\sin^2 \theta/2)^{1/1.16}$ for $M=3.12 \times 10^6$.

Table I. Wavelengths used.

	in vacuo (Å)	refractive index in acetone	in acetone (Å)
G	5461	1.3665	3996
V	4358	1.3674	3187
UV	3660	1.374	2664

Table II. Asymptotic behaviors.

	$M=5.9 \times 10^6$		$M=3.12 \times 10^6$	
	slope $\times 10^6$	$b^2/m^{1.16} (\text{\AA}^2)$	slope $\times 10^6$	$b^2/m^{1.16} (\text{\AA}^2)$
G	0.76	0.101	0.72	0.095
V	1.14	0.103	1.20	0.109
UV	1.72	0.116	1.70	0.114

Taking the intercepts as 0.074×10^{-6} and 0.140×10^{-6} for $M=5.9 \times 10^6$ shown in Fig. 3a and $M=3.12 \times 10^6$ in Fig. 3b, respectively, we can find the asymptotic slopes with the aid of Eq. (7a), and calculate the values of $b^2/m^{1.16}$, which are shown in Table II. The wavelength λ used is shown in Table I. The agreement of $b^2/m^{1.16}$ obtained from the asymptotic behaviors with Eq. (23) is fairly good.

Here we must deal with high molecular weight samples because the asymptotic behavior,

discussed in § 3, is to be well expected for $s^2\langle r_G^2 \rangle > 1$. Nevertheless, we must exclude the highest molecular weight sample of $M=7.8 \times 10^6$ because of its anomalous behavior, the cause of which is unclear.

In order to analyze the light scattering of unfractionated polymer, the effect of the polydispersity in the sample is discussed elsewhere.

The improvement of experimental accuracies will permit us to examine the non-Gaussian character of the polymer chain in more detail.

Appendix I.

$$\langle r_G^2 \rangle = \frac{1}{N^2} \sum_i \sum_j \langle r_{ij}^2 \rangle = b^2 N^{\epsilon-1} \sum_{i < j} \sum_{i < j} \left(\frac{j-i}{N} \right)^{1+\nu}, \quad (\text{A1})$$

where the substitution of integration for summation gives

$$\begin{aligned} \langle r_G^2 \rangle &= b^2 N^{1+\epsilon} \int_0^1 dx \int_0^x dy (x-y)^{1+\nu} = b^2 N^{1+\epsilon} \int_0^1 dx (1-x)x^{1+\nu} \\ &= \frac{b^2 N^{1+\epsilon}}{(2+\nu)(3+\nu)}. \end{aligned} \quad (\text{7a})$$

Appendix II.

Substituting integration for summation in the equation

$$P(\theta) = \frac{2}{N^2} \sum_i \sum_j \exp \left\{ -\frac{s^2}{6} b^2 N^{1+\epsilon} \left(\frac{j-i}{N} \right)^{1+\nu} \right\}, \quad (\text{A2})$$

we have

$$P(\theta) = 2 \int_0^1 dx (1-x) \exp \left(-\frac{s^2}{6} b^2 N^{1+\epsilon} x^{1+\nu} \right),$$

which can be written with the aid of substitution

$$t = ax^{1+\nu}, \quad a = \frac{s^2}{6} b^2 N^{1+\epsilon}, \quad (\text{A3})$$

$$P(\theta) \simeq \frac{2}{1+\nu} \int_0^\infty \frac{dt}{t} \left(\frac{t}{a} \right)^{1/1+\nu} \left\{ 1 - \left(\frac{t}{a} \right)^{1/1+\nu} \right\} e^{-t} = \frac{2}{1+\nu} \left(\frac{1}{a} \right)^{1/1+\nu} \left\{ \Gamma \left(\frac{1}{1+\nu} \right) - \left(\frac{1}{a} \right)^{1/1+\nu} \Gamma \left(\frac{2}{1+\nu} \right) \right\}.$$

This leads to

$$\frac{1}{P(\theta)} \simeq \frac{1+\nu}{2\Gamma(1/1+\nu)} \left\{ \frac{\Gamma(2/1+\nu)}{\Gamma(1/1+\nu)} + a^{1/1+\nu} \right\}. \quad (\text{10})$$

Appendix III.

$$P_1(\theta) = \frac{2}{N^2} \sum_i \sum_j \int_0^\infty \frac{\sin sr}{sr} W_{ij^1}(r) 4\pi r^2 dr = -\frac{2z}{N^{5/2}} \sum_{i < j} \sum_{k < l} (l-k)^{-3/2} \exp \left(-u \frac{\nu_{ij}}{N} \right), \quad (\text{A4})$$

where

$$u = \frac{N}{6} s^2 b^2$$

and

$$\nu_{ij} = \left\{ \begin{array}{ll} j-i & \text{if } 0 \leq k < l \leq i < j \leq N \text{ or } 0 \leq i < j < k < l \leq N \text{ (Region A) ,} \\ (j-i) - (l-k) & \text{if } 0 \leq i < k < l \leq j \leq N \text{ (Region B) ,} \\ (j-i) - \frac{(l-i)^2}{(l-k)} & \text{if } 0 \leq k \leq i < l \leq j \leq N \text{ (Region C) ,} \\ (j-i) - \frac{(j-k)^2}{(l-k)} & \text{if } 0 \leq i < k \leq j < l \leq N \text{ (Region D) ,} \\ (j-i) - \frac{(j-i)^2}{(l-k)} & \text{if } 0 \leq k \leq i < j < l \leq N \text{ (Region E) .} \end{array} \right\} \quad (12a)$$

These regions contribute to $P_1(\theta)$ as follows:

$$\left. \begin{array}{ll} \text{(A)} & -5.224zN^{1/2} \left(\frac{1}{u} - \frac{2}{u^2} \right) + o \left(\frac{1}{u^3} \right) , \\ \text{(B)} & -5.224zN^{1/2} \left(\frac{1}{u^2} \right) + o \left(\frac{1}{u^3} \right) , \\ \text{(C)} & -10.448zN^{1/2} \left(\frac{1}{u^2} \right) + o \left(\frac{1}{u^3} \right) , \\ \text{(D)} & -10.448zN^{1/2} \left(\frac{1}{u^2} \right) + o \left(\frac{1}{u^3} \right) , \\ \text{(E)} & -10.448zN^{1/2} \left(\frac{1}{u^2} \right) + o \left(\frac{1}{u^3} \right) , \end{array} \right\} \quad (A5)$$

where

$$\left. \begin{array}{l} \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} = 2.612 \\ \text{and} \\ \exp(-t^2) \int_0^x \exp(t^2) dt \simeq \frac{1}{2x} + \frac{1}{2^2 x^3} + \dots \quad \text{for } x \gg 1 \end{array} \right\} \quad (A6)$$

are used.

So we find for large u

$$\begin{aligned} \frac{1}{P(\theta)} &\simeq \left\{ 2 \left(\frac{1}{u} - \frac{1}{u^2} \right) - 5.224zN^{1/2} \left(\frac{1}{u} + \frac{5}{u^2} \right) \right\}^{-1} \\ &\simeq \frac{1}{2} \{ (1 + 18.284zN^{1/2} + \dots) + u(1 + 2.612zN^{1/2} + \dots) \} . \end{aligned} \quad (10b)$$

Appendix IV.

Expanding the exponential in the right side member of

$$W_0(r) = \frac{2}{N^2} \sum_{i < j} \left\{ \frac{3}{2\pi(j-i)b^2} \right\}^{3/2} \exp \left\{ -\frac{3r^2}{2(j-i)b^2} \right\} \quad (A7)$$

for $r \ll b$, we obtain in the aid of $n = j - i$

$$\begin{aligned} W_0(r) &= \frac{2}{N^2} \sum_{n=1}^N \left(\frac{3}{2\pi b^2} \right)^{3/2} \frac{N-n}{n^{3/2}} \left\{ 1 - \frac{3r^2}{2b^2 n} + \frac{1}{2} \left(\frac{3r^2}{2b^2 n} \right)^2 \mp \dots \right\} \\ &\simeq \frac{5.22}{N} \left(\frac{3}{2\pi b^2} \right)^{3/2} \left\{ 1 - 0.513 \left(\frac{3r^2}{2b^2} \right) + 0.214 \left(\frac{3r^2}{2b^2} \right)^2 \mp \dots \right\} , \end{aligned} \quad (13)$$

where Eq. (A6) and

$$\sum_{n=1}^{\infty} \frac{1}{n^{5/2}} = 1.341, \quad \sum_{n=1}^{\infty} \frac{1}{n^{7/2}} = 1.127 \quad (\text{A8})$$

are used¹²⁾.

On the other hand, using $x = (j-i)/N$ and integrating by parts, we find for $r \gg N^{1/2}b$

$$\begin{aligned} W_0(r) &\simeq 2 \left(\frac{3}{2\pi N b^2} \right)^{3/2} \int_0^1 dx \frac{1-x}{x^{3/2}} \exp \left(-\frac{3r^2}{2Nb^2x} \right) \\ &\simeq 2 \left(\frac{3}{2\pi N b^2} \right)^{3/2} \left(\frac{2Nb^2}{3r^2} \right)^2 \exp \left(-\frac{3r^2}{2Nb^2} \right) \left\{ 1 - 3 \left(\frac{2Nb^2}{3r^2} \right) + \frac{45}{4} \left(\frac{2Nb^2}{3r^2} \right)^2 \mp \dots \right\}. \end{aligned} \quad (\text{13a})$$

Appendix V.

$$P_1(\theta) = \int_0^\infty \frac{\sin sr}{sr} 4\pi r^2 dr \int_0^\infty G(x) e^{-rx} dx \quad (\text{A9})$$

can be calculated for large s as

$$P_1(\theta) = 8\pi \int_0^\infty dx G(x) \frac{x}{(x^2 + s^2)^2} = -8\pi \left\{ \frac{1}{s^4} W_1'(0) - \frac{2}{s^6} W_1'''(0) + \dots \right\},$$

where

$$W_1'(0) = - \int_0^\infty dx x G(x), \quad W_1'''(0) = - \int_0^\infty dx x^3 G(x) \quad (\text{A10})$$

as used. Thus we can have

$$\begin{aligned} \frac{1}{P(\theta)} &\simeq \left\{ 2 \left(\frac{1}{u} - \frac{1}{u^2} \right) - \frac{8\pi}{s^4} W_1'(0) \right\}^{-1} \\ &= \frac{1}{2} \left[\left\{ 1 + \frac{\pi(Nb^2)^2}{9} W_1'(0) \right\} + u + \dots \right]. \end{aligned} \quad (\text{17})$$

References

- 1) P. Debye: J. Phys. and Coll. Chem. **51** (1947) 18.
- 2) B. H. Zimm: J. Chem. Phys. **16** (1948) 1093.
- 3) H. Tompa: *Polymer Solution* (Butterworths Sci. Publ., 1956).
- 4) A. J. Hyde, J. H. Ryan and F. T. Wall: J. Polymer Sci. **23** (1958) 129.
- 5) A. Peterlin: J. Chem. Phys. **23** (1955) 2464.
- 6) H. Mizutani: J. Phys. Soc. Japan **11** (1956) 245. Y. Miyake: *Busseiron-Kenkyû* No. 104 (1957) 49.
- 7) O. B. Ptitzyn: Z. Fiz. Khim. **31** (1957) 1091.
- 8) M. Fixman: J. Chem. Phys. **23** (1955) 1656.
- 9) H. Yamakawa and M. Kurata: J. Phys. Soc. Japan **13** (1958) 78. M. Kurata, H. Yamakawa and E. Teramoto: J. Chem. Phys. **28** (1958) 785.
- 10) E. Teramoto, M. Kurata, R. Chûjô, C. Suzuki, K. Tani and T. Kajikawa: J. Phys. Soc. Japan **10** (1955) 953.
- 11) H.-J. Cantow and G. V. Schulz: Z. phys. Chem. (N. F.) **1** (1954) 365; **2** (1954) 117.
- 12) E. Jahnke and F. Emde: *Funktionentafeln* (B. G. Teubner, 1933) 323.

Influence of the Molecular Weight Distribution on the Polymer Properties

By Akira MIYAKE

*Department of Physics, Faculty of Liberal Arts and Science,
Shizuoka University*

and Hatsuko ADACHI

Fujieda-Nishi High School, Shizuoka Prefecture

(Received December 5, 1959)

The Schulz-Zimm expression of the molecular weight distribution in a polymer sample is conveniently extended in terms of associated Laguerre polynomials. Applying the present expression, the authors investigate the influence of the molecular weight distribution especially on the osmotic pressure and on the intra- and intermolecular light scattering. The second virial coefficients in the osmotic pressure expression and in the intermolecular light scattering function for the polydisperse polymer are examined.

§ 1. Introduction

The molecular weight distribution in a polymer sample affects the physicochemical properties of the polymer.^{1),2)} Recently much improved accuracies of the measurements have made it possible to show the discrepancy in various average molecular weights obtained by various kinds of measurement, *e.g.* the number average molecular weight $\bar{M}_n$ obtained from the osmotic pressure measurement differs from the weight average one $\bar{M}_w$ from the light scattering, the Z average one $\bar{M}_z$ from the sedimentation, or the viscosity average one $\bar{M}_v$ from the intrinsic viscosity for one and the same sample. The discrepancy in them must give a key to a secret of the molecular weight distribution in the sample.

The influence of the molecular weight distribution has been investigated for the mechanical relaxation by Fujita and Ninomiya³⁾ and for the diffusion constant by Daune *et al.*⁴⁾ But for the osmotic pressure and the light scattering studies, it is necessary to investigate this influence in more detail.

Now, let the weight fraction of those polymer molecules with the molecular weight between M and $M+dM$ in the sample be $f(M)dM$. $f(M)$ is called the molecular weight distribution function of the sample and is usually unknown function unless any test measurement is made. In order to analyze the effect of the molecular weight distribu-

tion, we have been accustomed to use the expression presented by Schulz⁵⁾ and Zimm⁶⁾ for $f(M)$:

$$f(M) = AM^z \exp(-\beta M), \quad (1.1)$$

where z and β are adjustable parameters, A is the normalizing factor determined by the equation

$$\int_0^\infty f(M) dM = 1 = \frac{A}{\beta^{z+1}} \Gamma(z+1), \quad (1.2)$$

where $\Gamma(z)$ is the Gamma function. Then, as $f(M)dM/M$ is proportional to the number fraction, we obtain

$$\bar{M}_n = 1 / \int_0^\infty \frac{1}{M} f(M) dM = \frac{z}{\beta} \quad (1.3)$$

and similarly

$$\begin{aligned} \bar{M}_w &= \int_0^\infty M f(M) dM = \frac{z+1}{\beta} = \frac{z+1}{z} \bar{M}_n, \\ \bar{M}_z &= \int_0^\infty M^2 f(M) dM / \int_0^\infty M f(M) dM \\ &= \frac{z+2}{\beta} = \frac{z+2}{z} \bar{M}_n, \\ \bar{M}_{z+1} &= \int_0^\infty M^3 f(M) dM / \int_0^\infty M^2 f(M) dM \\ &= \frac{z+3}{\beta} = \frac{z+3}{z} \bar{M}_n, \end{aligned} \quad (1.3')$$

etc..

Furthermore, when the molecular weight dependence of the intrinsic viscosity is given by $[\eta] \propto M^\alpha$, we have

$$\begin{aligned}\bar{M}_v &= \left\{ \int_0^\infty M^\alpha f(M) dM \right\}^{1/\alpha} \\ &= \frac{1}{\beta} \left\{ \frac{\Gamma(z+\alpha+1)}{\Gamma(z+1)} \right\}^{1/\alpha} = \frac{1}{z} \left\{ \frac{\Gamma(z+\alpha+1)}{\Gamma(z+1)} \right\}^{1/\alpha} \bar{M}_n.\end{aligned}\quad (1.3'')$$

But, unfortunately Eq. (1.1) contains only two adjustable parameters, so that it is rarely consistent with the measured values of more than two quantities. Thus, the extension of Eq. (1.1) to be compatible with any measured values is quite desirable. It is the purpose of the present article to find such a useful expression and to apply this to the analysis of osmotic pressure and light scattering measurements.

§ 2. Expression of $f(M)$

Previously the authors⁷⁾ suggested to utilize the Laguerre polynomials as the bases of orthogonal expansion of $f(M)$.

The natural extension of Eq. (1.1) seems to be

$$f(M) = M^z \exp(-\beta M) \sum_{n=0}^{\infty} c_n L_n^{(z)}(\beta M) \quad z > 0, \quad (2.1)$$

where

$$L_n^{(z)}(x) = \sum_{k=0}^n \binom{n+z}{n+k} \frac{(-x)^k}{k!} \quad (2.2)$$

is the associated Laguerre polynomial of the n th order.⁸⁾

Using the orthogonal relation:⁸⁾ when $Re z > -1$

$$\left. \begin{aligned} \int_0^\infty e^{-x} x^z L_m^{(z)}(x) L_n^{(z)}(x) dx &= 0 \quad \text{for } m \neq n, \\ &= \Gamma(z+n+1)/n! \quad \text{for } m=n, \end{aligned} \right\} \quad (2.2')$$

we have

$$\int_0^\infty f(M) dM = 1 = \frac{c_0}{\beta^{z+1}} \Gamma(z+1). \quad (2.3)$$

And using the relation (see Appendix I)

$$L_n^{(z)}(x) = \sum_{k=0}^n (-1)^k \binom{y}{k} L_{n-k}^{(z+y)}(x), \quad (2.2'')$$

we can obtain

$$\left. \begin{aligned} \frac{1}{\bar{M}_n} &= \int_0^\infty \frac{1}{M} f(M) dM = \frac{\Gamma(z)}{\beta^z} \sum_{n=0}^{\infty} c_n, \\ \bar{M}_w &= \int_0^\infty M f(M) dM = \frac{\Gamma(z+2)}{\beta^{z+2}} (c_0 - c_1), \\ \bar{M}_z \cdot \bar{M}_w &= \int_0^\infty M^2 f(M) dM = \frac{\Gamma(z+3)}{\beta^{z+3}} (c_0 - 2c_1 + c_2), \end{aligned} \right\}$$

$$\begin{aligned}\bar{M}_{z+1} \cdot \bar{M}_z \cdot \bar{M}_w &= \int_0^\infty M^3 f(M) dM \\ &= \frac{\Gamma(z+4)}{\beta^{z+4}} (c_0 - 3c_1 + 3c_2 - c_3),\end{aligned}\quad (2.3')$$

etc.,

and also

$$\begin{aligned}\bar{M}_v^\alpha &= \int_0^\infty M^\alpha f(M) dM \\ &= \frac{\Gamma(z+\alpha+1)}{\beta^{z+\alpha+1}} \sum_{n=0}^{\infty} c_n (-1)^n \binom{\alpha}{n}.\end{aligned}\quad (2.3'')$$

Any average molecular weight obtained from the measurement of any other quantity proportional to M^α , e.g. sedimentation constant or diffusion constant, can be calculated similarly. So the more average values are known, the better the shape of $f(M)$ can be determined by means of Eqs. (2.3), (2.3') and (2.3''). Thus we can find Eq. (2.1) very convenient for a practical use.

§ 3. Influence on the Osmotic Pressure

The osmotic pressure Π in the monodisperse and dilute polymer solution can be expanded as

$$\Pi/RT = \frac{c}{M} + A_2 c^2 + \dots, \quad (3.1)$$

where R is the gas constant, T the absolute temperature, c the weight concentration of the polymer.

In the case of polydisperse polymer, we must replace the molecular weight M by $\bar{M}_n$ and the second virial coefficient A_2 by

$$\int_0^\infty \int_0^\infty A(M, M') f(M) f(M') dM dM', \quad (3.2)$$

where $A(M, M')$ is the second virial coefficient due to the interaction between the molecules with the molecular weight M and M' .⁹⁾

Recently the molecular weight dependence of A_2 has been reported by several authors.¹⁰⁻¹³⁾ And the recalculation of $A(M, M')$ in the case of $M \neq M'$ according to the theories by Albrecht¹⁴⁾ and by Yamakawa and Kurata¹⁵⁾ gives

$$\begin{aligned}A(M, M') &= A_2^0 [1 - 1.067 \mu \{ 2(M^{3/2} M'^{-1} \\ &\quad + M^{-1} M'^{3/2}) + 5(M^{1/2} + M'^{1/2}) \\ &\quad - 2(M + M')^{5/2} M^{-1} M'^{-1} \} + \dots],\end{aligned}\quad (3.3)$$

where

$$A_2^0 = -\frac{N_0}{2m^2} \int_0^\infty \left[1 - \exp \left\{ -\frac{\varphi(r)}{kT} \right\} \right] 4\pi r^2 dr \quad (3.4)$$

is independent of M , N_0 is the Loschmidt number, m the molar weight per segment, $\varphi(r)$ the intersegment potential energy, and

$$\mu = \left(\frac{3}{2\pi b^2} \right)^{3/2} \frac{1}{m^{1/2}} \int_0^\infty \left[1 - \exp \left\{ -\frac{\varphi(r)}{kT} \right\} \right] 4\pi r^2 dr$$

$$= - \left(\frac{3m}{\pi b^2} \right)^{3/2} \frac{A_2^0}{2^{1/2} N_0}, \quad (3.5)$$

b the segment length. Using Eqs. (2.1), (3.2) and (3.3), we can obtain

$$A_2 = A_2^0 [1 - 2.134\mu \{ 2(\overline{M}^{3/2}/\overline{M}_n) + 5\overline{M}^{1/2} - (\overline{M} + \overline{M}')^{5/2}/\overline{MM}' + \dots \}], \quad (3.2')$$

where

$$\overline{M}^\gamma = \int_0^\infty M^\gamma f(M) dM = \frac{\Gamma(z+\gamma+1)}{\beta^{\gamma+\gamma+1}} \sum_{n=0}^\infty c_n (-1)^n \binom{\gamma}{n} \quad (3.6)$$

and (cf. Appendix II)

$$\frac{(\overline{M} + \overline{M}')^{5/2}/\overline{MM}'}{\overline{MM}'} = \int_0^\infty \int_0^\infty \frac{(M + M')^{5/2}}{MM'} f(M) f(M') dM dM'$$

$$= \frac{2^{5/2} \Gamma(z) \Gamma\left(z + \frac{5}{4}\right) \Gamma\left(z + \frac{7}{4}\right)}{\beta^{2z+(5/2)} \Gamma\left(z + \frac{1}{2}\right)} \left\{ c_0^2 - \frac{1}{2} c_0 c_1 \right.$$

$$- \frac{3}{8} \left(\frac{3z+4}{2z+1} \right) c_1^2 + \frac{1}{8} \left(\frac{7z+11}{2z+1} \right) c_0 c_2$$

$$- \frac{9}{32} \left(\frac{3z+4}{2z+1} \right) c_1 c_2$$

$$\left. + \frac{1}{32} \left(\frac{23z+34}{2z+1} \right) c_0 c_3 + \dots \right\}. \quad (3.7)$$

Eq. (3.2') shows a complicated dependence of A_2 on the molecular weight distribution.

§ 4. Influence on the Intramolecular Light Scattering

The intensity of excess scattering $I(\theta)$ at the scattering angle θ is given in the very dilute and monodisperse polymer solution by

$$I(\theta) \propto McP(\theta) + o(c^2), \quad (4.1)$$

where $P(\theta)$ is the intramolecular scattering function, which has been examined by one of the authors.¹⁶⁾

In the case of polydisperse polymer, we must replace $McP(\theta)$ in Eq. (4.1) as

$$I(\theta) \propto c \int_0^\infty M f(M) P_M(\theta) dM + o(c^2), \quad (4.1')$$

where $P_M(\theta)$ is the scattering function corresponding to the molecular weight M .

I) Initial Behavior of $c/I(\theta)$

For small values of $s = (4\pi/\lambda) \sin(\theta/2)$

$$P_M(\theta) = 1 - \frac{s^2}{3} \langle r_M^2 \rangle + o(s^4), \quad (4.2)$$

where λ is the wavelength of light in the solution, $\langle r_M^2 \rangle$ the mean square radius of gyration from the center of mass, having the molecular weight M , given according to the assumption by Wall *et al.*¹⁷⁾ by

$$\langle r_M^2 \rangle = \frac{b^2 M^{1+\varepsilon}}{(2+\nu)(3+\nu)m^{1+\varepsilon}} \quad \varepsilon \geq \nu, \quad (4.3)$$

ε and ν being constants. Then Eq. (4.1') can be written as

$$I(\theta) \propto c \left\{ \overline{M}_w - \frac{s^2 b^2 \overline{M}^{2+\varepsilon}}{3(2+\nu)(3+\nu)m^{1+\varepsilon}} + o(s^4) \right\} + o(c^2), \quad (4.4)$$

which leads to

$$\lim_{c \rightarrow 0} Kc/I(\theta) = \frac{1}{\overline{M}_w} \left\{ 1 + \frac{s^2 b^2 \overline{M}^{2+\varepsilon}}{3(2+\nu)(3+\nu)m^{1+\varepsilon} \overline{M}_w} + o(s^4) \right\}, \quad (4.5)$$

where K is the constant including the factor $1 + \cos^2 \theta$. If $\varepsilon = \nu = 0$, then Eq. (4.5) is reduced to⁶⁾

$$\lim_{c \rightarrow 0} Kc/I(\theta) = \frac{1}{\overline{M}_w} \left\{ 1 + \frac{s^2 b^2}{18m} \overline{M}_z + o(s^4) \right\}. \quad (4.5a)$$

On the other hand, according to the theories by Fixman¹⁸⁾ and by Yamakawa and Kurata¹⁵⁾

$$\langle r_M^2 \rangle = \frac{b^2 M}{6m} (1 + 1.276\mu M^{1/2} - 2.077\mu^2 M + \dots), \quad (4.3')$$

from which we find

$$\lim_{c \rightarrow 0} Kc/I(\theta) = \frac{1}{\overline{M}_w} \left\{ 1 + \frac{s^2 b^2}{18m} (\overline{M}_z + 1.276\mu \overline{M}^{5/2}/\overline{M}_w - 2.077\mu^2 \overline{M}_{z+1} \cdot \overline{M}_z + \dots) + o(s^4) \right\}. \quad (4.5')$$

II) Asymptotic Behavior of $c/I(\theta)$

For sufficiently large values of s , according to the assumption by Wall *et al.*¹⁷⁾ we have¹⁶⁾

$$P_M(\theta) \cong \frac{2}{1+\nu} \left(\frac{6m^{1+\varepsilon}}{s^2 b^2 M^{1+\varepsilon}} \right)^{1/(1+\nu)} \left\{ I'(1/(1+\nu)) - \left(\frac{6m^{1+\varepsilon}}{s^2 b^2 M^{1+\varepsilon}} \right)^{1/(1+\nu)} I'(2/(1+\nu)) \right\}, \quad (4.6)$$

and we find

$$I(\theta) \propto \frac{2c}{1+\nu} \left(\frac{6m^{1+\varepsilon}}{s^2 b^2} \right)^{1/1+\nu} \left\{ \overline{M}^{(\nu-\varepsilon)/(1+\nu)} \Gamma(1/1+\nu) - \overline{M}^{(\nu-2\varepsilon-1)/(1+\nu)} \left(\frac{6m^{1+\varepsilon}}{s^2 b^2} \right)^{1/1+\nu} \Gamma(2/1+\nu) \right\}, \quad (4.7)$$

which leads to

$$\lim_{c \rightarrow 0} Kc/I(\theta) \cong \frac{1+\nu}{2\Gamma(1/1+\nu)\overline{M}^{(\nu-\varepsilon)/(1+\nu)}} \times \left\{ \frac{\Gamma(2/1+\nu)\overline{M}^{(\nu-2\varepsilon-1)/(1+\nu)}}{\Gamma(1/1+\nu)\overline{M}^{(\nu-\varepsilon)/(1+\nu)}} + \left(\frac{s^2 b^2}{6m^{1+\varepsilon}} \right)^{1/1+\nu} \right\}. \quad (4.8)$$

If $\varepsilon=\nu=0$, Eq. (4.9) is reduced to¹⁹⁾

$$\lim_{c \rightarrow 0} Kc/I(\theta) \cong \frac{1}{2} \left(\frac{1}{\overline{M}_w} + \frac{s^2 b^2}{6m} \right). \quad (4.8a)$$

On the other hand, according to the theories by Fixman,¹⁸⁾ Yamakawa and Kurata¹⁵⁾ we have¹⁶⁾

$$P_M(\theta) \cong 2 \left\{ \left(\frac{6m}{s^2 b^2 \overline{M}} \right) - \left(\frac{6m}{s^2 b^2 \overline{M}} \right)^2 \right\} - 5.224\mu \frac{\overline{M}}{m} \left\{ \left(\frac{6m}{s^2 b^2 \overline{M}} \right) + 5 \left(\frac{6m}{s^2 b^2 \overline{M}} \right)^2 \right\} + \dots. \quad (4.6')$$

Then we obtain

$$\lim_{c \rightarrow 0} Kc/I(\theta) \cong \frac{1}{2} \left\{ \frac{1}{\overline{M}_n} \left(1 + 13.06\mu \frac{\overline{M}_n}{m} + 5.224\mu \frac{\overline{M}_w}{m} + \dots \right) + \frac{s^2 b^2}{6m} \left(1 + 2.612\mu \frac{\overline{M}_w}{m} + \dots \right) \right\}. \quad (4.8')$$

§ 5. Influence on the Intermolecular Light Scattering

When the intermolecular scattering contribution is taken into account, we have for the monodisperse polymer^{20,21)}

$$I(\theta) \propto McP(\theta) - 2A_2 c^2 P_2(\theta) + o(c^3), \quad (5.1)$$

where $P_2(\theta)$ is the bimolecular scattering function given by Albrecht²¹⁾ as

$$P_2(\theta) = Q(\theta) P_M(\theta)^2,$$

$$Q(\theta) = 1 - 11.69s^2 \langle r_M^2 \rangle \mu M^{1/2} + \dots. \quad (5.2)$$

In the case of polydisperse polymer, we have $P_M(0)=1$ and $P_2(0)=1$, and for small values of θ we find²²⁾

$$I(o) \propto c \int_0^\infty Mf(M) dM - 2c^2 \int_0^\infty \int_0^\infty A(M, M') Mf(M) M'f(M') dM dM'$$

which is reduced to

$$Kc/I(o) = \frac{1}{\overline{M}_w} + 2A_2 c + \dots, \quad (5.3)$$

where A_2 is given by

$$A_2 = \frac{1}{\overline{M}_w^2} \int_0^\infty \int_0^\infty A(M, M') Mf(M) M'f(M') dM dM' \quad (5.4)$$

instead of Eq. (3.2). Using Eqs. (2.1), (3.3) and (5.4), we obtain

$$A_2 = A_2^0 [1 - 2.134\mu \{ 2(\overline{M}^{5/2}/\overline{M}_w^2) + 5(\overline{M}^{3/2}/\overline{M}_w) - (\overline{M} + \overline{M}')^{5/2}/\overline{M}_w^2 \} + \dots], \quad (5.4')$$

where

$$\begin{aligned} \overline{(\overline{M} + \overline{M}')^{5/2}} &= \int_0^\infty \int_0^\infty (\overline{M} + \overline{M}')^{5/2} f(\overline{M}) f(\overline{M}') d\overline{M} d\overline{M}' \\ &= \frac{2^{5/2} \Gamma(z+1) \Gamma\left(z + \frac{9}{4}\right) \Gamma\left(z + \frac{11}{4}\right)}{\beta^{2z+(9/2)} \Gamma\left(z + \frac{3}{2}\right)} \\ &\times \left\{ c_0^2 - \frac{5}{2} c_0 c_1 + \frac{15}{8} \left(\frac{z+1}{2z+3} \right) c_1^2 \right. \\ &+ \frac{15}{8} \left(\frac{z+2}{2z+3} \right) c_0 c_2 - \frac{15}{32} \left(\frac{z+1}{2z+3} \right) c_1 c_2 \\ &\left. - \frac{5}{32} \left(\frac{z+3}{2z+3} \right) c_0 c_3 + \dots \right\}. \end{aligned}$$

The authors are indebted to Mr. R. Chûjô for helpful discussions.

Appendix I.

Putting in the addition theorem of the associated Laguerre polynomials:⁸⁾

$$L_n^{(\alpha+\beta+1)}(x_1+x_2) = \sum_{k=0}^n L_{n-k}^{(\alpha)}(x_1) L_k^{(\beta)}(x_2), \quad (A1)$$

$\alpha=z+y$, $\beta=-(y+1)$, $x_1=x$ and $x_2=0$, we have

$$\begin{aligned} L_n^{(z)}(x) &= \sum_{k=0}^n L_{n-k}^{(z+y)}(x) L_k^{(-y-1)}(o) \\ &= \sum_{k=0}^n (-1)^k \binom{y}{k} L_{n-k}^{(z+y)}(x), \end{aligned} \quad (2.2')$$

where

$$L_k^{(-y-1)}(o) = \binom{k-y-1}{k} = (-1)^k \binom{y}{k} \quad (A2)$$

is used.

Appendix II.

Putting $x+y=s$ and $xy=t$, and using Eq. (2.2), we have

$$\begin{aligned}
 L_0^{(z)}(x)L_0^{(z)}(y) &= 1, \\
 L_0^{(z)}(x)L_1^{(z)}(y) + L_1^{(z)}(x)L_0^{(z)}(y) &= 2(1+z) - s, \\
 L_1^{(z)}(x)L_1^{(z)}(y) &= (1+z)^2 - (1+z)s + t, \\
 L_0^{(z)}(x)L_2^{(z)}(y) + L_2^{(z)}(x)L_0^{(z)}(y) &= (2+z)(1+z) - (2+z)s + \frac{1}{2}(s^2 - 2t), \\
 L_0^{(z)}(x)L_3^{(z)}(y) + L_3^{(z)}(x)L_0^{(z)}(y) &= \frac{(3+z)(2+z)(1+z)}{3} - \frac{(3+z)(2+z)}{2}s + \frac{3+z}{2}(s^2 - 2t) - \frac{1}{6}(s^3 - 3st), \\
 L_1^{(z)}(x)L_2^{(z)}(y) + L_2^{(z)}(x)L_1^{(z)}(y) &= (2+z)(1+z)^2 - \frac{3(2+z)(1+z)}{2}s + (3+z)t + \frac{1+z}{2}s^2 - \frac{1}{2}st, \\
 \text{etc..}
 \end{aligned} \tag{A3}$$

And we can find for arbitrary $\alpha > 0$ and $\beta > -1$

$$\int_0^\infty dx \int_0^\infty dy e^{-s} s^\alpha t^\beta = 2 \int_0^\infty e^{-s} s^\alpha ds \int_0^{s^{2/4}} dt \frac{t^\beta}{\sqrt{s^2 - 4t}} = \frac{\sqrt{\pi}}{2^{2\beta+1}} \frac{\Gamma(\alpha+2\beta+2)\Gamma(\beta+1)}{\Gamma\left(\beta+\frac{3}{2}\right)}. \tag{A4}$$

References

- 1) P. J. Flory: *Principles of Polymer Chemistry*. (Cornell Univ. Press, 1953).
- 2) N. Saitô: *Kôbunshi-Butsurigaku*. (High Polymer Physics, in Japanese) Shôkabô (1958).
- 3) H. Fujita and K. Ninomiya: *J. Polymer Sci.* **24** (1957) 233.
- 4) M. Daune, H. Benoit and Ch. Sadron: *J. Polymer Sci.* **16** (1955) 483. M. Daune and L. Freund: *ibid.* **23** (1957) 115. L. Freund and M. Daune: *ibid.* **29** (1958) 161.
- 5) G. V. Schulz: *Z. phys. Chem.* **B, 43** (1939) 25.
- 6) B. H. Zimm: *J. Chem. Phys.* **16** (1948) 1093, 1099.
- 7) A. Miyake and H. Adachi: *Kagaku* **29** (1959) 255; A. Miyake: *Repts. Liberal Arts & Science Fac. Shizuoka Univ. (Nat. Sci.)* **2** (1959) 135.
- 8) W. Magnus and F. Oberhettinger: *Formeln und Sätze für die speziellen Funktionen der mathematischen Physik*. (Springer, 1948) 108.
- 9) B. H. Zimm: *J. Chem. Phys.* **14** (1946) 164.
- 10) P. Outer, C. I. Carr and B. H. Zimm: *J. Chem. Phys.* **18** (1950) 830.
- 11) W. R. Krigbaum and P. J. Flory: *J. Amer. Chem. Soc.* **75** (1953) 5254. W. R. Krigbaum: *ibid.* **76** (1954) 3758.
- 12) C. E. H. Bawn and M. A. Wajid: *J. Polymer Sci.* **12** (1953) 109. C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin: *Trans. Faraday Soc.* **46** (1950) 862.
- 13) V. N. Tsvetkov, K. Z. Fattahov and O. V. Kallistov: *J. Exp. Theor. Phys. (USSR)* **26** (1954) 351.
- 14) A. C. Albrecht: *J. Chem. Phys.* **27** (1957) 1002.
- 15) H. Yamakawa: *J. Phys. Soc. Japan* **13** (1958) 87. M. Kurata and H. Yamakawa: *J. Chem. Phys.* **29** (1958) 311.
- 16) A. Miyake: *J. Phys. Soc. Japan* (in press)
- 17) A. J. Hyde, J. H. Ryan and F. T. Wall: *J. Polymer Sci.* **23** (1958) 129.
- 18) M. Fixman: *J. Chem. Phys.* **23** (1955) 1656.
- 19) H. Benoit: *J. Polymer Sci.* **11** (1953) 507.
- 20) P. J. Flory and A. M. Bueche: *J. Polymer Sci.* **27** (1958) 219.
- 21) A. C. Albrecht: *J. Chem. Phys.* **27** (1957) 1014.
- 22) A. Miyake: *Repts. Liberal Arts Fac. Shizuoka Univ. (Nat. Sci.)* no. 7 (1955) 19.

Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO

By Kazuko MOTIZUKI

Department of Physics, Osaka University, Japan

(Received January 6, 1960)

The NMR of Co^{59} in CoO is calculated, taking into account the interaction between the nuclear spin and the spin moment and residual orbital moment of the cobalt ion, beside the Fermi-type hyperfine interaction. The calculated frequency is 1028 Mc. The interaction between the nuclear quadrupole moment, Q , and the electric field gradient at the nucleus splits this resonance line into seven equally spaced lines. For a assumed value of $Q=0.5 \times 10^{-24} \text{ cm}^{-1}$, the line splitting is 6 Mc. The dependence of the frequency of the resonance lines on the direction of the applied field is also investigated. It is shown that by observing this dependence the angle of inclination of the spin axis to the tetragonal axis can be deduced. Further, theory of the indirect coupling between nuclear spins through hyperfine interaction and exchange interaction is developed, using the molecular field approximation. The line width arising from this indirect coupling is estimated to be 0.115 Mc, which is small compared with the line splitting.

§1. Introduction

Jaccarino¹⁾ reported recently a direct observation of the high frequency NMR of Co^{59} in single crystal of CoF_2 , in the frequency range of 160–190 Mc and in external field extending to 10 koe and at temperature 1.3° to 4.2°K . This high frequency resonance was due to the intra-atomic hyperfine interaction between the nuclear magnetic moment of Co^{59} and the unbalanced d -electrons on the Co^{2+} ion. A similar resonance can be expected for CoO and the present paper is concerned with the theoretical estimate of it.

CoO is antiferromagnetic with a Néel point at 290°K . It has a NaCl type structure with slight contraction ($\sim 1\%$) below the Néel temperature, along one of the cubic principal axes relative to the other two. The spin arrangement determined by neutron diffraction by Shull, Strauser and Wollan²⁾ and Roth³⁾ is such that the sheets of plus spins and minus spins alternate along one of the body diagonals. The axis of the spins deviates from the tetragonal axis by about 10° , in the direction away from the trigonal axis of the spin arrangement.^{4,5)}

This substance is particularly interesting since its Co ions have large residual orbital moments as studied theoretically in detail by Kanamori.⁵⁾ We expect the NMR of Co^{59} to occur in CoO at higher frequencies than in CoF_2 . In CoO , beside there being a hyper-

fine interaction of the Fermi-type, which is predominant in CoF_2 , the residual orbital moment of the Co^{2+} ion produces a strong internal magnetic field at its nucleus. There is also an interaction between the electric field gradient at the nucleus due to the non-spherical charge distribution of the d -electrons and the quadrupole moment of the nucleus, as in the case of CoF_2 , and this interaction gives rise to a splitting of the resonance line into seven lines. Since the electronic distribution can be calculated using Kanamori's theory and with the known radial function of the d -electron, the nuclear quadrupole moment of Co^{59} can be deduced by observing these line separations. Application of a magnetic field will split the lines into two groups, corresponding to the two antiferromagnetic sublattices, and this splitting will depend on the direction of the applied field. By observing them, it should be possible to deduce the angle of inclination of the spin axis relative to the tetragonal axis, although the existence of twin and magnetic domain structure will complicate the observation.

In this paper, we first derive in §2 the effective Hamiltonian for the nuclear spin of Co^{59} in CoO and estimate its frequency, neglecting the small inclination of the spin axis to the tetragonal axis. Then the effect of this inclination on the NMR lines is estimated in §3. It turns out, however, that this effect

is small. In §4, the NMR with an applied magnetic field is studied and further the possibility of determining the angle of inclination is discussed. In §5, the theory of the line width is developed and it is shown that the estimated width is small enough to allow for the observation of the line splitting due to the nuclear quadrupole moment and the line shift due to an applied field.

The line width of the NMR of an antiferromagnet, developed by Nakamura⁶⁾ and Suhli⁷⁾, arises from an indirect coupling between the nuclear spins through the hyperfine interaction and the exchange interaction between neighboring ions. They used the spin wave approximation, which cannot directly be applied to the present case, since in CoO the spin and orbital moments strongly couple each other and the orbital moment gives rise to a large anisotropy energy. A theory based on the molecular field approximation seems to be more appropriate in such a case.

§2. Effective Hamiltonian for the Nuclear Spin

The interaction between the Co^{59} nucleus and the surrounding electrons consists of the interaction between the nuclear magnetic moment, $\mathbf{I}$, and the magnetic field produced at the nucleus by the orbital and spin angular momenta of the electrons, the contact or Fermi interaction between $\mathbf{I}$ and the slightly unbalanced spins of the 3s and 2s electrons, and the interaction between the quadrupole moment, e^2Q , of the nucleus and the electric field gradient due to the electrons. It can be written⁸⁾

$$H = 2\gamma\beta\beta_N \sum_k \left[\left\{ \frac{(\mathbf{l}_k - \mathbf{s}_k) \cdot \mathbf{I}}{r_k^3} + \frac{3(\mathbf{r}_k \cdot \mathbf{s}_k)(\mathbf{r}_k \cdot \mathbf{I})}{r_k^5} \right\} + \frac{8\pi}{3} \delta(\mathbf{r}_k) \mathbf{s}_k \cdot \mathbf{I} \right] + \frac{e^2Q}{2I(2I-1)} \sum_k \left\{ \frac{I(I+1)}{r_k^3} - \frac{3(\mathbf{r}_k \cdot \mathbf{I})^2}{r_k^5} \right\} \quad (2.1)$$

$$\equiv H_l + H_a + H_F + H_Q,$$

where

$$H_l = 2\gamma\beta\beta_N \sum_k \frac{\mathbf{l}_k \cdot \mathbf{I}}{r_k^3}$$

$$H_a = 2\gamma\beta\beta_N \sum_k \left\{ \frac{-\mathbf{s}_k \cdot \mathbf{I}}{r_k^3} + \frac{3(\mathbf{r}_k \cdot \mathbf{s}_k)(\mathbf{r}_k \cdot \mathbf{I})}{r_k^5} \right\}$$

$$H_F = 2\gamma\beta\beta_N \sum_k \frac{8\pi}{3} \delta(\mathbf{r}_k) \mathbf{s}_k \cdot \mathbf{I}$$

$$H_Q = \frac{e^2Q}{2I(2I-1)} \sum_k \left\{ \frac{I(I+1)}{r_k^3} - \frac{3(\mathbf{r}_k \cdot \mathbf{I})^2}{r_k^5} \right\}.$$

Here the sum $\sum_k$ extends over all the electrons of the ion, $\mathbf{l}_k$ and $\mathbf{s}_k$ stand for the orbital and spin angular momentum of the k -th electron, respectively, r_k the distance of the k -th electron from the nucleus, β the Bohr magneton, β_N the nuclear magneton, γ the nuclear gyromagnetic factor in units of $e/2Mc$, and $\mathbf{I}$ the nuclear spin angular momentum of magnitude $7/2$. To obtain the effective Hamiltonian for the nucleus, the interaction (2.1) has to be averaged with respect to the electronic wave function of the ground state of the Co^{2+} ion.

The electronic state of the free Co^{2+} is $(3d)^7 {}^4F$. In the cubic crystalline field of CoO , the orbital degeneracy of this state is partially lifted leaving the ground state triply degenerate. This ground state can be described in terms of the angular momentum operator $\mathbf{l}$ of magnitude one, the total angular momentum $\mathbf{L}$ being replaced by $-(3/2)\mathbf{l}$. This small $\mathbf{l}$ is coupled to the spin angular momentum, $\mathbf{S}$, through the spin-orbit coupling and they form the total angular momentum $\mathbf{l} + \mathbf{S}$. The eigen-states of the ion are characterized by the eigen-values of $(\mathbf{l} + \mathbf{S})^2 = j(j+1)$, with $j = 1/2, 3/2, 5/2$. However, there exists exchange interaction among the ions, and when this is taken into account in the approximation of the Weiss molecular field, those states which have different j but equal $l_z + S_z$ couple each other, where z is the direction of the Weiss field. With this idea, Kanamori⁶⁾ calculated the wave function on the ground state of Co^{2+} ion at absolute zero, taking into account the effect of the small tetragonal deformation of the crystal. In his calculation the direction of the spins was simply assumed to be along $[001]$, i.e., the direction of the contraction. The Hamiltonian used by him is

$$H = 2J_1 z_1 \langle S \rangle S_z + \lambda' \mathbf{l} \cdot \mathbf{S} - c l_z^2 \quad (2.2)$$

and the ground state wave function was determined self-consistently as the lowest eigen-state of this Hamiltonian. In this expression, J_1 (>0) is the exchange interaction constant between next-nearest neighboring ions, z_1 the number of next-nearest neighbors

($z_1=6$), and $\lambda'=(-3/2)\lambda$, λ being the usual spin-orbit coupling constant. The ground state wave function thus determined was of the form

$$\psi_g = k_1\psi_{3/2,-1} + k_2\psi_{1/2,0} + k_3\psi_{-1/2,1}, \quad (2.3)$$

where the first and second suffices of ψ represent the values of S_z and I_z , respectively, and k_1 , k_2 and k_3 are numerical factors which depend on the magnitude of J_1 , λ' and the deformation coefficient c ($=140\text{ cm}^{-1}$). Using the values of $2J_1z_1=180\text{ cm}^{-1}$, $\lambda'=270\text{ cm}^{-1}$ and $c=140\text{ cm}^{-1}$, k_1 , k_2 and k_3 were calculated to be

$$k_1=0.909, \quad k_2=-0.385, \quad k_3=0.162. \quad (2.4)$$

Now, averaging the interaction (2.1) with respect to the wave function (2.3), the effective Hamiltonian for the nuclear spin takes the form

$$H_N = \xi_0 I_z + \eta_0 I_z^2, \quad (2.5)$$

where

$$\xi_0 = 2\gamma\beta\beta_N \left\langle \frac{1}{r^3} \right\rangle (k_l + k_a) + F, \quad (2.6)$$

$$\eta_0 = \frac{e^2 Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle k_Q.$$

F being the contact interaction with the inner $3s$ and $2s$ electrons and k_l , k_a and k_Q constants which are proportional to the averages of H_l , H_a and H_Q with respect to ψ_g . They are given by

$$k_l = -\frac{1}{2}(k_1^2 - k_3^2)(3 - 5\gamma^2),$$

$$k_a = -\frac{1}{7} \left[\frac{1}{5}(2 - 9\gamma^2 + 12\gamma\sqrt{1-\gamma^2}) \right. \\ \left. \times (k_1^2 - 2k_2^2 - k_3^2/3) + \frac{\sqrt{2}}{10}(1 + 13\gamma^2 \right. \\ \left. + 16\gamma\sqrt{1-\gamma^2})(\sqrt{3}k_1 - 2k_3)k_2 \right],$$

$$k_Q = \frac{3}{35}(2 - 9\gamma^2 + 12\gamma\sqrt{1-\gamma^2}) \\ \times (k_1^2 - 6k_2^2 + k_3^2), \quad (2.7)$$

where γ represents that amplitude of the ^4P wave function which is mixed by configuration interaction to the ground orbital triplet arising from ^4F ($\gamma=0.185$ according to Kanamori). Using k_1 , k_2 and k_3 given by (2.4), the numerical values of k_l , k_a and k_Q are calculated to be

$$k_l = -1.131, \quad k_a = -0.0437, \quad k_Q = 0.2051. \quad (2.8)$$

We will represent the term $\xi_0 I_z$ as

$$\xi_0 I_z = -\gamma\beta_N I_z (H_l + H_a + H_F) \quad (2.9)$$

and calculate the magnitudes of the effective fields H_l , H_a and H_F corresponding to k_l , k_a and F . Using $\langle 1/r^3 \rangle = 5.2 \times a_0^{-3}$, which is obtained from the hyperfine structure observation of the paramagnetic resonance⁹⁾, we have

$$H_l = 7.32 \times 10^5 \text{ oe} \\ H_a = 0.282 \times 10^5 \text{ oe}. \quad (2.10)$$

H_F can be described as¹⁰⁾

$$H_F = -A\bar{S}/\gamma\beta_N,$$

where $\bar{S}$ is the average value of the electron spin angular momentum with respect to ψ_g and, according to Kanamori, $\bar{S}=1.280$. A is the hyperfine constant (usually represented as $-P\kappa$). According to Abragam, Horowitz and Pryce,⁹⁾ $-A/\gamma=5.3 \times 10^{-3}\text{ cm}^{-1}$ for the free Co^{2+} ion. So,

$$H_F = 2.69 \times 10^5 \text{ oe}. \quad (2.11)$$

The total field acting on the cobalt nucleus is therefore

$$H_l + H_a + H_F = 10.29 \times 10^5 \text{ oe}. \quad (2.12)$$

Next we estimate the quadrupole interaction constant η_0 . Putting $Q=n \times 10^{-24}\text{ cm}^{-1}$, leaving n as yet unknown because the quadrupole moment of Co^{59} has not yet been determined, η_0 in units of field becomes

$$\eta_0 = 6.6n \times 10^3 \text{ oe}. \quad (2.13)$$

The nuclear spin state of Co^{59} is split into eight states by the Hamiltonian (2.5), the level separations being unequal due to the quadrupole interaction $\eta_0 I_z^2$. Therefore seven resonance lines should appear whose frequencies are distributed symmetrically about the central line with equal spacings. The frequency of the central line, ν_0 , is determined by ξ_0 . Using Eq. (2.12), we have

$$\nu_0 = 1028 \text{ Mc}. \quad (2.14)$$

The line separation, Δ , is $2\eta_0$ and is proportional to Q . Taking for instance $n=0.5$, i.e., $Q=0.5 \times 10^{-24}\text{ cm}^{-1}$, Δ is given by

$$\Delta = 6 \text{ Mc}. \quad (2.15)$$

If the line width is narrow enough compared with Δ to allow for the observation, it should be possible to determine the value of Q except for its sign.

§ 3. Effect of the Spin Axis Deviation from [001] on the NMR of Co^{59}

The ground state wave function of Co^{2+} , given by (2.3), was calculated on the assumption that the spin is along one of the cubic axes, [001], along which a small contraction of the crystal has taken place. However, we know from the analysis^{(4), (8)} of the neutron diffraction measurements that the spin orientation deviated from [001] by about 10° in the direction away from the trigonal axis, [111], of the spin arrangement. This spin inclination will modify the wave function of the ground state and so also the effective field acting on the nucleus.

First we shall consider the modification of the ground state wave function. We take [001] to be the z -axis. The spin direction will be denoted by z' , and we take the y' -axis perpendicular to the z' -axis in the plane formed by [110] and z' ; the x' -axis is perpendicular to the both. The angle between z' and z is denoted by α .

In calculating the ground state wave function, we note that the unperturbed Hamiltonian H_0 can be given by (2.2) and the unperturbed ground state wave function by (2.3), provided that z is replaced by z' for the both. The perturbed Hamiltonian is then

$$H' = -c(l_{x'}l_{y'} + l_{y'}l_{z'})\alpha + c(l_{z'}^2 - l_{y'}^2)\alpha^2 \\ \equiv H'_1\alpha + H'_2\alpha^2, \quad (3.1)$$

which is the difference between cl_z^2 and $cl_{z'}^2$, neglecting higher terms than α^2 . The wave functions and the corresponding energies of the excited states of H_0 have been obtained by Tachiki⁽¹¹⁾ and they are given in Appendix. With the perturbation method, the ground state wave function can be given as

$$\psi'_0 = \psi_0 + \alpha\psi_1^{(1)} + \alpha^2(\psi_1^{(2)} + \psi_2^{(1)}), \quad (3.2)$$

where ψ_0 is the unperturbed wave function and $\psi_1^{(1)}$, $\psi_1^{(2)}$ are obtained from the first order

and second order perturbations of H'_1 and $\psi_2^{(1)}$ from the first order perturbation of H'_2 .

Now, averaging the interaction (2.1) with respect to ψ'_0 , the effective Hamiltonian for the nucleus becomes

$$H_N = \xi I_{z'} + \eta I_{z'}^2 \mp \zeta I_y' \\ + \zeta'(I_{z'}I_{y'} + I_{y'}I_{z'}) + \zeta''(I^+I^+ + I^-I^-), \quad (3.3)$$

where ξ and η are different from ξ_0 and η_0 by terms proportional to α^2 and new terms with factors ζ , ζ' and ζ'' has been introduced, and $\mp$ corresponds to whether the spin axis deviation is away from or close to [111]. These coefficients are given by

$$\xi = 2\gamma\beta\beta_N \left\langle \frac{1}{r^3} \right\rangle [k_l + k_a + \alpha^2(k'_l + k'_a)] + F, \\ \eta = \frac{e^2Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle (k_q + \alpha^2k'_q), \\ \zeta = 2\gamma\beta\beta_N \left\langle \frac{1}{r^3} \right\rangle \alpha(k'_l + k'_a), \\ \zeta' = \frac{e^2Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle \alpha k''_q, \\ \zeta'' = \frac{e^2Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle \alpha^2 k_q. \quad (3.4)$$

k'_l , k'_l , k'_a , k'_a , k'_q , k'_q and k''_q are proportional to the averages of H_l , H_a and H_q with respect to ψ'_0 . Of these, the only non-negligible quantities are

$$k'_l = 0.127, \quad k'_l = 0.205, \quad k'_q = 0.055, 4. \quad (3.5)$$

Regarding the ζ and ζ' terms in (3.3) as perturbations, the energy levels of the nuclear spin ($I=7/2$) correct to second order can be calculated easily. The calculated frequencies of the seven resonance lines and also their line separations are given in Table I. The frequency of the central line is $\xi + (1/2\xi)(\xi^2 - 60\xi'^2)$. The seven lines are not equally spaced and they appear asymmetrically around the central line. However, the deviations from the equal spacing are very small, being proportional to ξ'^2/ξ and so proportional

Table I. The frequencies of the seven resonance lines of Co^{59} ($I=7/2$) and their line separation.

$m \leftrightarrow m-1$	frequencies of the resonance lines	line separations
$\pm 7/2 \leftrightarrow \pm 5/2$	$\xi + 6\eta + (\xi^2 \pm 36\zeta\xi' + 156\xi'^2)/2\xi$	$2\eta + (6\zeta\xi' \pm 60\xi'^2)/\xi$
$\pm 5/2 \leftrightarrow \pm 3/2$	$\xi + 4\eta + (\xi^2 \pm 48\zeta\xi' + 36\xi'^2)/2\xi$	$2\eta + (6\zeta\xi' \pm 36\xi'^2)/\xi$
$\pm 3/2 \leftrightarrow \pm 1/2$	$\xi + 2\eta + (\xi^2 \pm 12\zeta\xi' - 36\xi'^2)/2\xi$	$2\eta + (6\zeta\xi' \pm 12\xi'^2)/\xi$
$+1/2 \leftrightarrow -1/2$	$\xi - (\xi^2 - 60\xi'^2)/2\xi$	

to α^2 ; taking $\alpha=10^\circ$, the deviations are only 10^{-5} times the spacing. The part of ξ which is proportional to α^2 gives a uniform shift of the seven lines. For $\alpha=10^\circ$, this shift is

$$\Delta\nu = \frac{\nu_0}{430} \quad (3.6)$$

where ν_0 is the frequency of the central line for $\alpha=0$, given by (2.14).

§4. The NMR of Co^{59} under Application of a Magnetic Field

In this section we investigate the frequency change of the NMR of Co^{59} due to external magnetic field.

The ground state of each Co ion is affected by the applied field and also by the molecular field arising from the field-induced spin moments of the surrounding ions. To calculate the ground state wave function, we take the unperturbed Hamiltonian to be (2.2) with z replaced by z' , and the perturbing Hamiltonian to be

$$H' = \beta H \cdot (g_s S^{(+)} + g_l I^{(+)} + \sum_{h=x', y', z'} [2J_1 z_1 (\partial \langle S_h^{(-)} \rangle + J_2 z_2 (\partial \langle S_h^{(-)} + \delta \langle S_h^{(+)} \rangle)] S_h^{(+)} \quad (4.1)$$

where we consider the ion on the $+$ sublattice, and $\partial \langle S_h^{(+)} \rangle$, $\partial \langle S_h^{(-)} \rangle$ represent the induced spin moments of the ions on the $+$ and $-$ sublattices, respectively; $2J_1 z_1$ ($=180\text{cm}^{-1}$) and $2J_2 z_2$ ($=115\text{cm}^{-1}$) are the constants of exchange interactions with the next-nearest neighbor spins and the nearest neighbor spins. The induced moments are determined self-consistently as follows¹¹⁾:

$$\begin{aligned} \partial \langle S_h^{(+)} \rangle &= \partial \langle S_h^{(-)} \rangle \\ &= \frac{-2\beta(g_s \alpha_h + g_l \gamma_h)}{1 + 4Jz\alpha_h} H_h (h=x', y', z'), \end{aligned} \quad (4.2)$$

where

$$\begin{aligned} \alpha_h &= \sum_i \frac{|\langle g | S_h | i \rangle|^2}{E_i - E_g}, \\ \gamma_h &= \sum_i \frac{\langle g | S_h | i \rangle \langle i | I_h | g \rangle}{E_i - E_g}, \end{aligned} \quad (4.3)$$

and g and i represent the ground state, (2.2), and excited states (see Appendix); $g_s=2.161$, $g_l=-1.415$, and $2Jz=2J_1 z_1 + 2J_2 z_2$. The numerical values of α_h and γ_h calculated by Tachiki are

$$\begin{aligned} \alpha_{z'} &= 0.063, 3 & \gamma_{z'} &= -0.063, 3 \\ \alpha_{x'} &= \alpha_{y'} = 0.002, 26 & \gamma_{x'} &= \gamma_{y'} = -0.001, 22. \end{aligned}$$

Then, Eq. (4.1) can be written

$$H' = \beta g_l (H_{z'} I_{z'} + H_{x'} I_{x'} + H_{y'} I_{y'}) + \beta (g'_s H_{z'} S_{z'} + g''_s H_{x'} S_{x'} + g''_s H_{y'} S_{y'}) \quad (4.4)$$

$$\begin{aligned} g'_s &= g_s - 4Jz \frac{g_s \alpha_{z'} + g_l \gamma_{z'}}{1 + 4Jz\alpha_{z'}} = -1.321, \\ g''_s &= g_s - 4Jz \frac{g_s \alpha_{x'} + g_l \gamma_{x'}}{1 + 4Jz\alpha_{x'}} = 1.061. \end{aligned} \quad (4.5)$$

As the result of the perturbation, the ground state wave function takes the form

$$\begin{aligned} \psi_g &= \psi_g + \beta H_{z'} (k'_1 \psi_{3/2, -1} + k'_2 \psi_{1/2, 0} + k'_3 \psi_{-1/2, 1}) \\ &\quad + \beta H_{x'} (k'_4 \psi_{3/2, 0} + k'_5 \psi_{1/2, 1} + k'_6 \psi_{-1/2, -1} \\ &\quad + k'_7 \psi_{-1/2, 0} + k'_8 \psi_{-3/2, 1}) \\ &\quad - i\beta H_{y'} (k'_4 \psi_{3/2, 0} + k'_5 \psi_{1/2, 1} - k'_6 \psi_{-1/2, -1} \\ &\quad - k'_7 \psi_{-1/2, 0} - k'_8 \psi_{-3/2, 1}) \\ &\quad + (\beta H_{z'})^2 (k''_1 \psi_{3/2, -1} + k''_2 \psi_{1/2, 0} \\ &\quad + k''_3 \psi_{-1/2, 1}). \end{aligned} \quad (4.6)$$

The effective Hamiltonian for the nucleus consists of the average of the interaction (2.1) with respect to (4.6) and the direct interaction between the nuclear spin and the external field, $-\gamma \beta_N H \cdot I$:

$$\begin{aligned} H_N &= [\xi_0 + \xi'_H \beta H_{z'} + \xi''_H (\beta H_{z'})^2] I_{z'} \\ &\quad + [\gamma_0 + \gamma'_H \beta H_{z'} + \gamma''_H (\beta H_{z'})^2] I_{z'}^2 \\ &\quad + \sum_{x', y'} \xi_H \beta H_{x'} I_{x'} + \sum_{x', y'} \kappa_H \beta H_{x'} (I_{z'} I_{x'} \\ &\quad + I_{x'} I_{z'}) - \gamma \beta_N H \cdot I. \end{aligned} \quad (4.7)$$

Here ξ_0 and γ_0 are given by (2.6) and

$$\xi'_H = 2\gamma \beta \beta_N \left\langle \frac{1}{r^3} \right\rangle 2(k_{l,H} + k_{a,H} + k_{F,H})$$

$$\xi''_H = 2\gamma \beta \beta_N \left\langle \frac{1}{r^3} \right\rangle (k'_{l,H} + k'_{a,H} + k'_{F,H})$$

$$\gamma'_H = \frac{e^2 Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle 2k_{Q,H}$$

$$\gamma''_H = \frac{e^2 Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle k'_{Q,H}$$

$$\xi_H = 2\gamma \beta \beta_N \left\langle \frac{1}{r^2} \right\rangle (k'_{l,H} + k'_{a,H} + k'_{F,H})$$

$$\kappa_H = \frac{e^2 Q}{2I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle k'_{Q,H} \quad (4.8)$$

The constants $k_{l,H}$, $k_{a,H}$, $k_{F,H}$, $k_{Q,H}$ are proportional to the averages of $H_l H_a$, $H_F H_Q$ with respect to ψ'_g and are evaluated to be

$$\begin{aligned}
k_{l,H} &= 4.68 \times 10^{-5} \text{ (1/cm}^{-1}\text{)}, & k'_{l,H} &= -5.62 \times 10^{-2} \text{ (1/cm}^{-1}\text{)}, & k''_{l,H} &= -1.72 \times 10^{-5} \text{ (1/cm}^{-2}\text{)} \\
k_{a,H} &= 0.657 \times 10^{-5} \text{ "}, & k'_{a,H} &= 0.193 \times 10^{-3} \text{ "}, & k''_{a,H} &= -0.230 \times 10^{-5} \text{ "} \\
k_{Q,H} &= -1.66 \times 10^{-5} \text{ "}, & k'_{Q,H} &= 0.919 \times 10^{-3} \text{ "}, & k''_{Q,H} &= 0.188 \times 10^{-5} \text{ "} \\
k_{F,H} &= 1.06 \times 10^{-5} \text{ "}, & k'_{F,H} &= 2.55 \times 10^{-3} \text{ "}, & k''_{F,H} &= -0.498 \times 10^{-5} \text{ "}.
\end{aligned} \quad (4.9)$$

Table II. The nuclear magnetic resonance frequencies of Co^{59} by application of a magnetic field.

$m \leftrightarrow m-1$	frequencies
$\pm 7/2 \leftrightarrow \pm 5/2$	$\xi_H \pm 6\gamma_H + [\{\zeta_H - \gamma(\beta_N/\beta)\}^2 \pm 36\{\zeta_H - \gamma(\beta_N/\beta)\}\kappa_H + 156\kappa_H^2]\beta^2 H_{\perp}^2/2$
$\pm 5/2 \leftrightarrow \pm 3/2$	$\xi_H \pm 4\gamma_H + [\{\zeta_H - \gamma(\beta_N/\beta)\}^2 \pm 24\{\zeta_H - \gamma(\beta_N/\beta)\}\kappa_H + 36\kappa_H^2]\beta^2 H_{\perp}^2/2$
$\pm 3/2 \leftrightarrow \pm 1/2$	$\xi_H \pm 2\gamma_H + [\{\zeta_H - \gamma(\beta_N/\beta)\}^2 \pm 12\{\zeta_H - \gamma(\beta_N/\beta)\}\kappa_H - 36\kappa_H^2]\beta^2 H_{\perp}^2/2$
$\pm 1/2 \leftrightarrow -1/2$	$\xi_H + [\{\zeta_H - \gamma(\beta_N/\beta)\}^2 - 60\kappa_H^2]\beta^2 H_{\perp}^2/2$

$$\xi_H = \xi_0 + \{\xi'_H - \gamma(\beta_N/\beta)\}\beta H_{\parallel} + \xi''_H \beta^2 H_{\parallel}^2$$

$$\gamma_H = \gamma_0 + \{\eta'_H - \gamma(\beta_N/\beta)\}\beta H_{\parallel} + \eta''_H \beta^2 H_{\parallel}^2$$

$H_{\parallel}$ and $H_{\perp}$ represent the parallel and perpendicular components to the spin direction, z' , of the external magnetic field.

In the above calculation, the Fermi-type hyperfine interaction, H_F , was simply assumed to be $\mathbf{AS} \cdot \mathbf{I}$ with the empirical value of A quoted in §2, and S was averaged respect to ϕ'_0 .

The energy levels and frequencies of the seven resonance lines calculated from (4.7) are shown in Table II. These resonance lines shift by the external field. The frequency shift of the central line is given by

$$\begin{aligned}
\Delta\nu_H &= \left(\xi'_H - \gamma \frac{\beta_N}{\beta}\right) \beta H \cos \phi + \xi''_H \beta^2 H^2 \cos^2 \phi \\
&+ \frac{1}{2\xi_0} \left[\left(\xi'_H - \gamma \frac{\beta_N}{\beta}\right)^2 - 60\kappa_H^2 \right] \beta^2 H^2 \sin^2 \phi,
\end{aligned} \quad (4.10)$$

where ϕ represents the angle between the spin direction and the external magnetic field. When $\phi=0$, this is

$$\Delta\nu_H(\parallel) = -\gamma\beta_N H + \xi'_H \beta H + \xi''_H \beta^2 H^2. \quad (4.11)$$

The first term, $-\gamma\beta_N H$, represents the shift due to the direct action of the external field, and the second and third terms are due to the induced orbital and the spin moments of the Co^{2+} ion. For $H=10,000$ oe, they are -10.13 Mc, $+0.038,2$ Mc, and $-0.003,4$ Mc, respectively, so that the latter two are very small. When $\phi=\pi/2$, the shift is

$$\Delta\nu_H(\perp) = \frac{1}{2\xi_0} \left[\left(\xi'_H - \gamma \frac{\beta_N}{\beta}\right)^2 - 60\kappa_H^2 \right] \beta^2 H^2 \quad (4.12)$$

which is $-0.065,5$ Mc for $H=10,000$ oe. Obviously, the shift occurs in the opposite direc-

tions for the two antiferromagnetic sublattices.

If the line width is narrow compared with $\Delta\nu_H$, we should be able to observe the frequency shift depending on the direction of

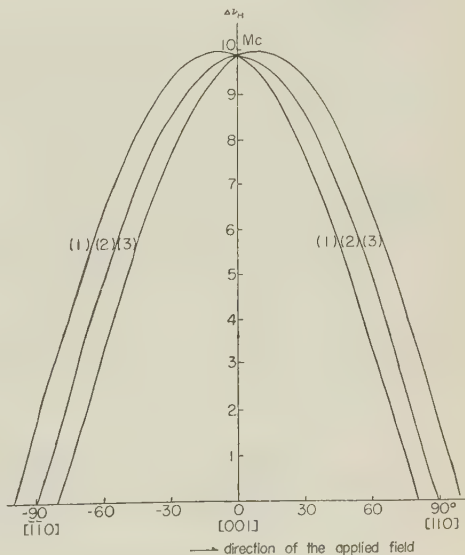


Fig. 1. The frequency shift curves for $H=10,000$ oe for four different domains having spin axes close to $[001]$. The field is rotated in the $(1\bar{1}0)$ plane.

Curve (1) for the domain whose spin axis is between $[001]$ and $[\bar{1}\bar{1}1]$, curve (3) for the domain whose spin axis $[001]$ and $[111]$, curve (2) for the domain whose spin axis is between $[001]$ and $[\bar{1}11]$ or $[1\bar{1}1]$.

applied field and thus in principle able to determine the spin direction relative to the tetragonal axis. However, if there are twin structures, many resonance lines will appear, which will complicate the analysis of the experimental results. The usual crystal may have twelve kinds of crystallographic domain, with trigonal axis along $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$ and $[\bar{1}1\bar{1}]$ and tetragonal axis along $[100]$, $[010]$ and $[001]$. In each domain, the direction of the spin axes is unique, but it differs for different domains. In Fig. 1., we show the frequency shift curves for four different domains having spin axes close to $[001]$ when the field ($=10,000$ oe) is applied in the (110) plane. These three curves are well separated compared with the theoretical line width ~ 0.115 Mc, which will be calculated in the next section. When the field is in the neighborhood of $[001]$, the spin axes of the other eight domains are almost perpendicular to the applied field and so the shifts of the resonance line arising from them will be very small.

§5. Line Width

One of the origins of the line width is the spin-lattice relaxation time T_1 . However, T_1 increases indefinitely with decreasing temperature, as was shown by Moriya¹²⁾ and van Kranendonk and Bloom.¹³⁾ For MnF_2 Shulman and Jaccarino¹⁴⁾ found a T_1 of about 20 sec at 4.2°K . We may therefore neglect the effect of T_1 for CoO at low enough temperatures.

The dominant origin of the line width can be the indirect coupling among nuclear spins through spin waves and hyperfine interaction,

as was shown by Nakamura⁶⁾ and Suhl⁷⁾ and in the case of MnF_2 . In their theories they used the spin wave theory and assumed the two-sublattice model of $+$ and $-$ spins in which the nearest neighbors of a spin of one sublattice belong to other sublattice and the exchange interaction acts only between nearest neighbors. These points have to be modified in applying to CoO.

The spin arrangement of CoO is rhombohedral and the rhombohedral unit cell contains a $+$ spin and a $-$ spin. The two-sublattice model is therefore applicable, but as shown by Kanamori,⁵⁾ the exchange interaction of one spin with the next-nearest neighbors ($2J_1z_1=180\text{cm}^{-1}$) is comparable to that with the nearest neighbors ($2J_2z_2=115\text{cm}^{-1}$). Furthermore, the Co ion has a residual orbital angular momentum and this produces a very large anisotropy energy. These facts (particularly the latter points) make it very difficult to formulate the spin wave theory in an unambiguous way.

Therefore, we shall here use the molecular field approximation to calculate the line width. The polarization of the electron spin system in CoO due to a nuclear spin through hyperfine interaction may be localized in a small region around that nucleus since the anisotropy energy of each electron spin is comparable to the exchange energy. So we may expect that the molecular field approximation is a good approximation.

Consider an ion pair of i and j . The wave functions and energy eigenvalues of the ground and excited states of each ion in the molecular field approximation are given by (2.3) and Appendix. For the pair of i and j we have

$$\begin{aligned} \text{ground state: } \phi_{00} &= \phi_0(i)\phi_0(j) \quad , \quad E_{00} = 2E_0 \\ \text{excited state: } \phi_{mk} &= \phi_m(i)\phi_k(j) \quad , \quad E_{mk} = E_m + E_k \\ & \quad (m \neq k, \quad m, k = 0, 1, 2, \dots, 11) \end{aligned} \quad (5.1)$$

If i and j are next-nearest neighbors, a part of the exchange interaction between them has already been taken into account by the molecular field to determine (5.1), so that we shall take

$$H_{ij} = 2J_1(S_i \cdot S_j - \langle S_{jz} \rangle S_{iz} - \langle S_{iz} \rangle S_{jz}) \quad (5.2)$$

as perturbation. If i and j are next nearest neighbors, the exchange interaction between

them

$$H_{ij} = 2J_2 S_i \cdot S_j \quad (5.3)$$

should fully be taken as perturbation. As the total perturbing Hamiltonian, we take the sum of the hyperfine Hamiltonians of the i and j ions and H_{ij} :

$$H' = H_i + H_{ij} + H_j \quad (5.4)$$

The effective Hamiltonian of the indirect coupling between the nuclear spins of i and j can be obtained by the third order perturbation. We obtain

$$\begin{aligned}
 H_{ij}^{eff} = & \sum_{(i,j)} \sum_{m,k} \left[\frac{\langle 0(i) | H_i | m(i) \rangle \langle m(i) | 0(j) | H_{ij} | 0(i) k(j) \rangle \langle k(j) | H_j | 0(j) \rangle}{(E_{m0} - E_{00})(E_{k0} - E_{00})} \right. \\
 & + \frac{\langle 0(i) | H_i | m(i) \rangle \langle 0(j) | H_j | k(j) \rangle \langle m(i) k(j) | H_{ij} | 0(i) 0(j) \rangle + c.c.}{(E_{m0} - E_{00})(E_{mk} - E_{00})} \\
 & \left. + \frac{\langle 0(i) | H_i | m(i) \rangle \langle 0(j) | H_j | 0(j) \rangle \langle m(i) 0(j) | H_{ij} | 0(i) 0(j) \rangle + c.c.}{(E_{m0} - E_{00})^2} \right] \\
 & - \frac{1}{2} \sum_{(i,j)} \sum_m \frac{1}{2} \frac{1}{(E_{m0} - E_{00})^2} \times \\
 & [\langle 0(i) | H_i | 0(i) \rangle \langle 0(i) 0(j) | H_{ij} | 0(i) m(j) \rangle \langle m(j) | H_j | 0(j) \rangle \\
 & + \langle 0(i) | H_i | 0(i) \rangle \langle 0(j) | H_j | m(j) \rangle \langle 0(i) m(j) | H_{ij} | 0(i) 0(j) \rangle] .
 \end{aligned} \quad (5.5)$$

Here $0(i)$ and $m(i)$ represent the ground and excited states of the i -th ion and $\sum_{(i,j)}$ indicates that the summation should be taken with i and j interchanged. After a calculation and neglecting the third and fourth order terms of I_i and I_j which are small, this effective Hamiltonian can be written in the form

$$H_{ij}^{eff} = \alpha_{ij} I_{iz} I_{jz} + \beta_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \quad (5.6)$$

The second moment is given, using Van Vleck's formula,¹⁵⁾ by

$$\langle (\hbar \Delta \omega)^2 \rangle_{av} = \frac{1}{3} I(I+1) \sum \alpha_{ij}^2 \quad (5.7)$$

Taking $\sum_j$ only over nearest neighbors and next-nearest neighbors, this becomes

$$\langle (\hbar \Delta \omega)^2 \rangle_{av} = \frac{1}{3} I(I+1) (12\alpha_{n,n}^2 + 6\alpha_{n,n,n}^2), \quad (5.8)$$

where

$$\begin{aligned}
 \alpha_{n,n} = & -3.532 \times 10^{-5} \times J_2 \\
 & \times \left(2r\beta\beta_N \left\langle \frac{1}{r^3} \right\rangle \right)^2 (1/\text{cm}^{-2})
 \end{aligned}$$

$$\begin{aligned}
 \alpha_{n,n,n} = & -4.571 \times 10^{-5} \times J_1 \\
 & \times \left(2r\beta\beta_N \left\langle \frac{1}{r^3} \right\rangle \right)^2 (1/\text{cm}^{-2})
 \end{aligned} \quad (5.9)$$

which are evaluated to be

$$\alpha_{n,n} = -2.39 \text{ oe}, \quad \alpha_{n,n,n} = -9.70 \text{ oe} \quad (5.10)$$

Therefore,

$$\sqrt{\langle (\hbar \Delta \omega)^2 \rangle_{av}} = 57.6 \text{ oe} \quad (5.11)$$

If a Gaussian shape is assumed for the absorption curve, the corresponding separation between the points of maximum slopes is $57.6 \times 2 = 115.2 \text{ oe}$ or 0.115 Mc . This is small compared with the quadrupolar splitting, 6 Mc (see (2.15)), and the line shift due to the applied field, $\Delta\nu_H (=10 \text{ Mc, for } 10,000 \text{ oe})$.

The writer would like to express her sincere thanks to Professor T. Nagamiya for encouragement and kind discussion. She is also indebted to Professor K. Yosida for valuable discussion and to Dr. M. Tachiki for communication of numerical results prior to publication.

Appendix

The Wave Functions and the Corresponding Energies of the Excited States of the Hamiltonian (2.2).

$$\begin{aligned}
 \phi_1 = & 0.837\phi_{1/2,-1} - 0.507\phi_{-1/2,0} + 0.204\phi_{-3/2,1} & \Delta E_1 = 402 \text{ cm}^{-1} \\
 \phi_2 = & 0.467\phi_{1/2,-1} + 0.468\phi_{-1/2,0} - 0.750\phi_{-3/2,1} & \Delta E_2 = 981 \\
 \phi_3 = & 0.285\phi_{1/2,-1} + 0.723\phi_{-1/2,0} + 0.629\phi_{-3/2,1} & \Delta E_3 = 1535 \\
 \phi_4 = & 0.817\phi_{3/2,0} - 0.577\phi_{1/2,1} & \Delta E_4 = 434 \\
 \phi_5 = & 0.577\phi_{3/2,0} + 0.817\phi_{1/2,1} & \Delta E_5 = 1096 \\
 \phi_6 = & 0.365\phi_{3/2,-1} + 0.543\phi_{1/2,0} - 0.756\phi_{-1/2,1} & \Delta E_6 = 596 \\
 \phi_7 = & 0.203\phi_{3/2,-1} + 0.746\phi_{1/2,0} + 0.634\phi_{-1/2,1} & \Delta E_7 = 1279 \\
 \phi_8 \text{ to } \phi_{11} = & \text{are unimportant in the present calculations.}
 \end{aligned}$$

References

- 1) V. Jaccarino: Phys. Rev. Letters **2** (1959) 163.
- 2) C. G. Shull, W. A. Strauser and E. Q. Wollan: Phys. Rev. **83** (1951) 333.
- 3) W. L. Roth: Phys. Rev. **110** (1958) 1333.
- 4) T. Nagamiya and K. Motizuki: Rev. Mod. Phys. **30** (1958) 89.
- 5) J. Kanamori: Progr. Theor. Phys. **17** (1957) 177, 197.
- 6) T. Nakamura: Progr. Theor. Phys. **20** (1958) 542.
- 7) H. Suhl: J. phys. radium. **20** (1959) 333.
- 8) A. Abragam and M. H. L. Pryce: Proc. Roy. Soc. A, **205** (1951) 135.
- 9) A. Abragam, J. Horowitz and M. H. L. Pryce: Proc. Roy. Soc. A, **230** (1955) 169.
- 10) W. Marshall: Phys. Rev. **110** (1958) 1280.
- 11) M. Tachiki: Private communication.
- 12) T. Moriya: Progr. Theor. Phys. **16** (1956) 23.
- 13) J. Van Kranendonk and M. Bloom: Physica, **22** (1956) 545.
- 14) R. G. Shulman and V. Jaccarino: Phys. Rev. **103** (1956) 1126.
- 15) J. H. Van Vleck: Phys. Rev. **74** (1948) 1168.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

Interaction between Rod-like Polyelectrolytes

By Tsuyoshi OHNISHI, Nobuhisa IMAI
and Fumio OOSAWA

*Department of Physics, Faculty of Science,
Nagoya University, Nagoya, Japan*

(Received January 7, 1960)

A system of rod-like polyelectrolytes in a salt-free solvent is treated systematically. The force between two rods arranged parallel in their free volume is obtained, as a function of their charge density and the distance between them, by using the exact solution of the Poisson-Boltzmann equation for this system and the general expression of force by Bell and Levine. Numerical examples are given under various conditions of charge and distance. At high charge, the force between charged rods is greatly depressed by counter ions around the rods even at the short mutual distance. Owing to the neutrality condition a force which we call the neutrality force appears between rods. This force makes stable the equidistant arrangement of many rods in the solution. Simpler models; plate, one rod, and pipe; are also treated and a general theory on the force in cylindrical coordinate systems is developed. As a result, the effect of counter ions on the force between charged particles is clearly understood.

§1. Introduction

In dilute solutions of rod-like particles such as tobacco mosaic virus a phase separation occurs at very low ionic strength. An ordered phase where the particles are arranged parallel appears at concentration higher than a critical value. Several authors¹⁾²⁾³⁾ concluded theoretically that this phase separation is mainly due to the excluded volume effect of very asymmetric particles. According to these theories, however, for the solution of tobacco mosaic virus molecules of axial ratio

15~20, the critical concentration becomes about 20% or more, which is considerably higher than the experimental value (Ca. 2%). This discrepancy is due to the neglect of the electrostatic interaction between the particles. Actually, the phase separation of tobacco mosaic virus is easily destroyed by addition of a small amount of salts⁴⁾ ($10^{-4} \sim 10^{-3}$ N).

It is necessary, therefore, to estimate theoretically the magnitude of this electrostatic interaction. The simple application of

the electric double layer theory brings the result of increasing the apparent thickness of rods and consequently can not explain the very low critical concentration observed in experiments. As another theoretical approach, the cylindrical free volume model per rod was applied to a solution of rod-like particles arranged parallel, and concluded the possibility of phase separation. This theory,⁵⁾ however, seems to make some mistakes in the calculation of free energy. For examining the validity of the free volume model per rod, it is desirable to analyse the interaction between two rods.

In this paper, we derive the force between two rods arranged parallel in their free volume by basing upon an exact solution of the Poisson-Boltzmann equation for this system.⁶⁾ The force is given as a function of the distance between rods and the charge density of rods, and the magnitude of the force is numerically calculated. The main results are (i) the great suppression of the repulsive force between rods by counter ions distributed around the rods, and (ii) the appearance of the neutrality force which makes stable the equidistant arrangement of many rods in solution.

In addition to the system of two parallel rods, we examine the force in some simpler models, i.e., plate model and pipe model. Further, we give a general treatment of the force in various two-dimensional systems. (one rod, pipe, and two rods). By these discussions, we can understand the important effect of counter ions on the force between charged colloidal particles. Although we can not yet deal with a solution of rod-like particles in an arbitrary non-parallel arrangement, the present results show the remarkable character of the electrostatic interaction between charged rods and the stability of the equidistant arrangement of these rods.

§ 2. Force on Charged Colloidal Particle

The force between charged colloidal particles can generally be obtained by differentiating the free energy of the system which is derived from the solution of the Poisson-Boltzmann equation by integration.⁷⁾ This derivation, however, becomes more and more difficult when the system becomes complicated, and for our system of two rod-like

polyelectrolytes the analytical integration seems to be impossible. In this paper, therefore, the force is obtained from the electric field by the method of Bell and Levine⁸⁾ without calculating the free energy of the system. These authors derived the following general expression of the force exerting on a particle in dispersion medium of electrolytes. In our problem we assume, simplicity, that the particle is rigid and the dielectric constant D is constant everywhere. When a particle β is by δa , the expression for the free energy variation is written as

$$\delta F = - \int_{s_\beta} X \delta a ds \quad (2.1)$$

where

$$-X = \{T - T^i - (\Pi - \Pi^i)U\} : n_s \quad (2.2)$$

$$T = (D/8\pi)[2EE - E^2 U] \quad (2.3)$$

Here, superfix i denotes the particle interior, and n_s is a unit normal vector of surface element ds drawn outwards from the dispersion medium, E the electric field vector, T the electrostatic stress tensor, U the second-order unit tensor. The terms Π indicates osmotic pressure by ions, which is approximately written as

$$\Pi = kT \sum_{i=1}^m C_i \quad (2.4)$$

where C_i is the number density (number/c.c.) of ions of type i ($i=1, 2, \dots, m$).

In some simple models, these expressions may be interpreted in the following way. As shown in Fig. 1, let a solution of one

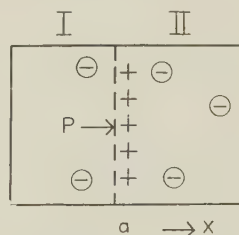


Fig. 1. Simple model interpretations.

species of counter ion be divided into two cells, I, II, by a positively charged membrane fixed at $x=a$. Then, in equilibrium a pressure difference P appears at the membrane. Denoting the counter ion and the molecule of the medium by suffices i and h , the equilibrium conditions can be expressed by chemical potentials μ as follows:

$$\begin{aligned} \mu_{h(x)} &= \frac{D}{8\pi} E_{(x)}^2 v_h + kT \ln(1 - \rho_{(x)}) + p_{(x)} v_h \\ &= \text{const.} \end{aligned} \quad (2.5)$$

$$\mu_{i(x)} = kT \ln \rho(x) - e\psi_{(x)} + p_{(x)} v_i = \text{const.} \quad (2.6)$$

where $\psi_{(x)}$, $E_{(x)}$, $\rho_{(x)}$, $-e$, $p_{(x)}$, v_h and v_i stand for potential, electric field, counter ion mole fraction, counter ion charge, pressure, partial molal volume of molecule and ion respectively.

In usual systems, the order estimation of values of various quantities gives $p \sim 10^6$, $\rho \sim 10^{-3}$, $v_h \sim v_i \sim 10^{-23}$, and $kT \sim e\psi \sim 10^{-14}$, and therefore the last term of (2.6) is negligible. Then, the equilibrium condition of the whole system can be described as

$$\frac{D}{8\pi} E_{(x)}^2 v_h - kT \rho_{(x)} + p_{(x)} v_h = \text{const.} \quad (2.7)$$

$$kT \ln \rho_{(x)} - e\psi_{(x)} = \text{const.} \quad (2.8)$$

$$\Delta\psi = +\frac{4\pi e}{D} c_{(x)} \quad (2.9)$$

$$P = p_{I(x)} - p_{II(x)} \quad (2.10)$$

where (2.9) is the Poisson equation, (2.10) pressure difference, and $c_{(x)}$ the number density of the counter ion.

The procedure of solving these equations is this: first, the Poisson-Boltzmann equation is obtained from (2.8) and (2.9) as

$$\Delta\psi = \kappa^2 e^{+e\psi/\kappa T} \quad (2.11)$$

where constant κ is the Debye-Hückel parameter determined by the normalization condition. When this Poisson-Boltzmann equation is exactly solved, by inserting the result to (2.7), we can easily derive the pressure $p_{(x)}$. Combining with (2.10), the pressure difference P is obtained as

$$P = \left\{ kTC_{(a)} - \frac{D}{8\pi} E_{(a)}^2 \right\}_I - \left\{ kTC_{(a)} - \frac{D}{8\pi} E_{(a)}^2 \right\}_{II} \quad (2.12)$$

For an infinitely thin membrane, the potential is continuous at $x=a$, and $C_{I(a)} = C_{II(a)}$. Then, we have

$$P = \frac{D}{8\pi} \{ E_{II(a)}^2 - E_{I(a)}^2 \}. \quad (2.13)$$

When the electric field at the surface of the particle is perpendicular to the surface, (2.1) is reduced to (2.12) or (2.13), and therefore the above simple thermodynamic interpretation is applicable. In general, however, nondiagonal components of the stress tensor T do not vanish, and the force must be calculated from (2.1).

§ 3. Simple Models

To understand intuitively the effect of the counter ions on the force between polyelectrolytes, we consider some simple models, namely parallel plates and coaxial pipes.

(1) Parallel plate model

Let two infinitely wide and thin plates bearing Ne positive charges per unit area be arranged parallel in their neutrality zone ($0 \leq r \leq l$) as shown in Fig. 2. It must be

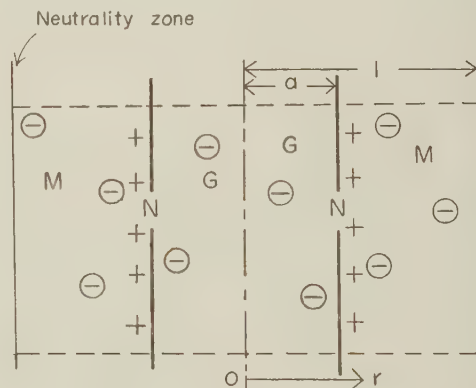


Fig. 2. Parallel plate model.

remembered that in the salt-free systems, it is necessary to set a certain neutrality zone. The zeropoint of the electric potential is chosen at the circumference of the neutrality zone through-out our calculation.

Here, we consider the right half of the system. Let numbers of counter ions inside and outside the plate be G and M . Clearly

$$N = G + M \quad (3.1)$$

and the Poisson-Boltzmann equation for this system becomes

$$\frac{d^2\phi}{dr^2} = \kappa^2 e^\phi \quad (3.2)$$

where

$$\phi = \frac{e\psi}{kT} \quad (3.3)$$

$$\kappa^2 = \frac{4\pi Ne^2}{DkT} \left[\int e^\phi dv \right]^{-1}. \quad (3.4)$$

This equation is solved under the boundary conditions

$$\phi|_{r=0} = 0 \quad (3.5)$$

$$\left(\frac{d\phi}{dr} \right)_{r=0} = \left(\frac{d\phi}{dr} \right)_{r=\tau} = 0. \quad (3.6)$$

and

$$\left. \begin{aligned} \left(\frac{d\phi^i}{dr} \right)_{r=a} &= + \frac{4\pi G e^2}{DkT} \equiv 2g \\ \left(\frac{d\phi^o}{dr} \right)_{r=a} &= - \frac{4\pi M e^2}{DkT} \equiv -2m \end{aligned} \right\} \quad (3.7)$$

where ϕ^i and ϕ^o mean the potentials inside and outside. The result becomes

$$\phi_{(r)}^i = -2 \ln \cos \eta r + 2 \ln \eta - \ln \frac{\kappa^2}{2}, \quad (0 \leq r \leq a) \quad (3.8)$$

$$\phi_{(r)}^o = -2 \ln \cos \delta(l-r), \quad (a \leq r \leq l) \quad (3.9)$$

$$\kappa^2 = 2\delta^2.$$

The parameters δ and η are determined by the following transcendental equations

$$\left. \begin{aligned} \delta \tan \delta(l-a) &= m \\ \eta \tan \eta a &= g \\ m+g &= n \equiv \frac{2\pi N e^2}{DkT} \end{aligned} \right\} \quad (3.10)$$

From (2.13), (3.3) and (3.7), the pressure becomes

$$P = \frac{2\pi e^2}{D} N(M-G). \quad (3.11)$$

This equation shows that the force originates in the difference between the numbers of counter ions in both sides. The point a_0 where the force vanishes (free energy minimum) becomes

$$a_0 = l/2 \quad (3.12)$$

independently of the net charge of the plate. This means that the equidistant arrangement of plates is most stable. The pressure is also expressed as

$$P = kT \{C_{(0)} - C_{(l)}\}. \quad (3.13)$$

This result can be derived from the free energy variation by the displacement of the two circumferences where $E=0$ ($r=0, l$) instead of moving the plates.

(2) Pipe model

Here let us consider an uniformly charged pipe (Fig. 3).

The pipe is infinitely long and thin and

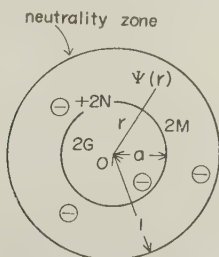


Fig. 3. Pipe model.

bears charge $2Ne$ per unit length. Putting

$$x=r/a, \quad L=l/a, \quad (3.14)$$

the Poisson-Boltzmann equation becomes

$$\frac{d^2\phi}{dx^2} + \frac{1}{x} \frac{d\phi}{dx} = \kappa^2 a^2 e^{\phi(x)}$$

$$\kappa^2 = \frac{8\pi N e^2}{DkT} \left[\int e^{\phi} dv \right]^{-1}. \quad (3.15)$$

This equation is solved under conditions similar to (3.5), (3.6) and (3.7), namely

$$\phi_{(L)}^o = 0 \quad (3.16)$$

$$\left(x \frac{d\phi^o}{dx} \right)_{x=L} = \left(x \frac{d\phi^i}{dx} \right)_{x=0} = 0 \quad (3.17)$$

$$\left. \begin{aligned} \left(x \frac{d\phi^i}{dx} \right)_{x=1} &= + \frac{4Ge^2}{DkT} \equiv +4\mu \\ \left(x \frac{d\phi^o}{dx} \right)_{x=1} &= - \frac{4Me^2}{DkT} \equiv -4\lambda \end{aligned} \right\} \quad (3.18)$$

The results are

$$\left. \begin{aligned} \phi_{(x)}^i &= -2 \ln \sinh [\ln x - \coth^{-1}(1+2\mu)] \\ &\quad -2 \ln \frac{x}{L} - \ln \frac{\kappa^2 l^2}{2}, \quad (0 \leq x \leq 1) \\ \phi_{(x)}^o &= -2 \ln \sinh \left[\delta \ln \frac{x}{L} + \frac{1}{2} \ln \frac{1-\delta}{1+\delta} \right] \\ &\quad -2 \ln \frac{x}{L} + \ln \delta^2 - \ln \frac{\kappa^2 l^2}{2}, \quad (1 \leq x \leq L) \\ \kappa^2 l^2 &= 2(1-\delta^2) \end{aligned} \right\} \quad (3.19)$$

where δ is determined by the transcendental equation

$$\left. \begin{aligned} \delta \ln L &= \coth^{-1}(H/\delta) - \coth^{-1}(1/\delta) \\ H &= 1-2\lambda \end{aligned} \right\} \quad (3.20)$$

When $2N$ is small, δ is real, but with increasing $2N$, δ changes into imaginary, i.e.

$$\delta \rightarrow 0 \rightarrow i\delta. \quad (3.21)$$

The pressure exerting on the pipe is

$$P = \frac{D}{8\pi} \{E_{0(a)}^2 - E_{l(a)}^2\}$$

$$= \frac{1}{2\pi a} \frac{4e^2 N(M-G)}{Da} \equiv - \left(\frac{\partial F}{\partial (\pi a^2)} \right)_l \quad (3.22)$$

and it becomes zero at $M=G$. But in this case, the minimum point a_0 where $P=0$ depends on the charge as

$$\left. \begin{aligned} a_0 &\rightarrow l/\sqrt{2} \quad (N \rightarrow 0) \\ a_0 &\rightarrow l \quad (N \rightarrow \infty) \end{aligned} \right\} \quad (3.23)$$

Equation (3.22) is transformed into

$$- \left(\frac{\partial F}{\partial a} \right)_l = \frac{D}{a} \left(\frac{kT}{e} \right)^2 \{4\nu - (1-\delta^2)\} \quad (3.24)$$

$$= \frac{2kT\pi l^2}{a} \{\bar{C} - C_{(l)}\} \quad (3.25)$$

where

$$\bar{C}=2N/\pi l^2. \quad (3.26)$$

This means that the force is proportional to the difference between the mean density and the density at the circumference.

The present results for the pipe model can readily be applied to the one-rod model by putting G equal to zero. These expressions will be compared with the result in the two rod-like polyelectrolytes in the following sections.

§ 4. Interaction between Two Rods

The problem of a single rod-like polyelectrolyte system was exactly treated by Fuoss, Lifson, and Katchalsky⁹; Alfrey, Berg and Morawetz¹⁰; and by Imai and Oosawa¹¹. The problem of the interaction between two rods, however, has not yet been solved, because in this system the Poisson-Boltzmann equation becomes a non-linear partial differential equation. Fortunately, we have succeeded in solving this equation for the system of two parallel rods bearing uniform surface charge Ne per unit length,⁶ and therefore, we can derive the force between these parallel rods. Derivation and analysis of the solution of the Poisson-Boltzmann equation will be presented in details by one of the authors (N.I.) in the other paper¹². Here we write down only the final solution briefly.

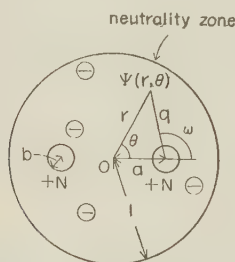


Fig. 4. Two rods.

As shown in Fig. 4, two infinitely long rods (radius b) are arranged parallel at distance $2a$ in their free volume of radius l . When we put

$$r/a=x, \quad l/a=L \quad \text{and} \quad b/a=B \quad (4.1)$$

the Poisson-Boltzmann equation of the system is written as

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{1}{x} \frac{\partial \phi}{\partial x} + \frac{1}{x^2} \frac{\partial^2 \phi}{\partial \theta^2} = \kappa^2 a^2 e^{\phi(x, \theta)} \quad (4.2)$$

and the boundary conditions as

$$\begin{aligned} &(\text{surface charge density on each rod}) = \text{const.} \\ &\phi(L, 0) = 0, \quad \oint \left(x \frac{\partial \phi}{\partial x} \right)_{x=L} d\theta = 0. \end{aligned} \quad (4.3) \quad (4.4)$$

The solution is written as

$$\phi = \begin{cases} -2 \ln [E_0 \tau^{1/2-\varepsilon/2} F_1 F_1^* - F_0 \tau^{1/2+\varepsilon/2} F_2 F_2^*], & |1-t| \leq 1 \\ -2 \ln [D_0 \tau^{1/2-\varepsilon/2} F_3 F_3^* - C_0 \tau^{1/2+\varepsilon/2} F_4 F_4^*], & |1-t| \geq 1 \end{cases} \quad (4.5) \quad (4.6)$$

where

$$\tau = (1-t)(1-t^*), \quad t = x^2 e^{2i\theta}, \quad t^* = x^2 e^{-2i\theta}. \quad (4.7)$$

Here, $F_{1,2,3,4}$ signify hypergeometric functions

$$\left. \begin{aligned} F_1 &= F(\alpha, \beta, \alpha + \beta + \frac{1}{2}, 1-t) \\ F_2 &= F(\frac{1}{2} - \alpha, \frac{1}{2} - \beta, \frac{3}{2} - \alpha - \beta, 1-t) \\ F_3 &= F(\beta, \frac{1}{2} - \alpha, \beta - \alpha + 1, 1/(1-t)) \\ F_4 &= F(\alpha, \frac{1}{2} - \beta, \alpha - \beta + 1, 1/(1-t)) \end{aligned} \right\} \quad (4.9)$$

and

$$\left. \begin{aligned} \alpha &= 1/4 - \varepsilon/2 - \delta/4 \\ \beta &= 1/4 - \varepsilon/2 + \delta/4 \end{aligned} \right\} \quad (4.9)$$

F^* is obtained by changing t in F into t^* .

If $L \gg 1$, the boundary condition (4.4) may be written as

$$\phi(L, \theta) = 0, \quad \left(x \frac{\partial \phi}{\partial x} \right)_{x=L} = 0. \quad (4.10)$$

In this case δ and ε are determined by the following transcendental equations

$$\frac{1+\delta}{1-\delta} L^{2\varepsilon} = \frac{\Gamma^2(\alpha-\beta) \Gamma(\frac{1}{2}-\alpha) \Gamma(1-\alpha) \Gamma(\frac{1}{2}+\beta) \Gamma(\beta)}{\Gamma^2(\beta-\alpha) \Gamma(\frac{1}{2}-\beta) \Gamma(1-\beta) \Gamma(\frac{1}{2}+\alpha) \Gamma(\alpha)} \quad (4.11)$$

$$1-\nu = \varepsilon \coth \left\{ \frac{1}{2} \ln (E_0/F_0) - \varepsilon \ln 2B \right\} \quad (4.12)$$

where

$$\nu = \frac{Ne^2}{DkT}, \quad F_0 = \frac{1}{E_0} \frac{\kappa^2 a^2}{32\varepsilon^2} \quad (4.13)$$

$$\kappa^2 a^2 = \frac{2(1-\delta^2)}{L^2}. \quad (4.14)$$

Constant ν gives the charge density along the rod and $\nu=1$ corresponds to one electronic charge per 7 Å of rod in water at room temperature. According to our numerical calculations, (4.10) is approximately satisfied even for $L \approx 2$ (see § 5).

Constants C_0 , D_0 are determined by (4.10), and E_0 by analytical continuation by which the potentials (4.5) and (4.6) are exactly connected. If the charge is small, δ and ε are both real. But with increasing charge,

first δ alone changes into imaginary, and finally, both become imaginary. It must be noted here that the solution of the Poisson-Boltzmann equation of this system is the function of the ratios x , L and B .

When the radius of the rods becomes infinitely thin, the transcendental equation (4.12) becomes

$$\epsilon = 1 - \nu \quad (B \rightarrow 0) \quad (4.15)$$

and the result is reduced to the case described in the previous paper⁶⁾. In this case, there is no solution for $\nu > 1$. This fact shows the counter ion condensation around rod-like polyelectrolytes and excess charges $\nu - 1$ are compensated by counter ions on the rods.

For simplicity, we assume thin rods for which

$$B \ll 1 \quad (4.16)$$

and obtain the free energy variation δF_1 for the displacement of a rod. Let (q, ω) be the polar coordinate from the center of the rod, then the osmotic term in (2.1) becomes

$$\begin{aligned} \delta F_{1(\text{osm})} &= - \int \Pi U : n_s \delta a ds \\ &= kT \int C \cos \omega ds \delta a \\ &= \frac{D}{a} \left(\frac{kT}{e} \right)^2 \cdot O(B^{2\epsilon}) \delta a. \end{aligned} \quad (4.17)$$

The term from the electric field inside the particle becomes $O(B^2)$. Therefore, these terms can be neglected when $B \rightarrow 0$. Then, transforming (2.1), we have for the free energy change

$$\delta F_{1(\text{el})} = \frac{D}{8\pi} \left[-2 \int_{s_1} \frac{\partial \psi}{\partial n_s} E \delta a ds - \int_{s_1} E^2 n_s \delta a ds \right] \quad (4.18)$$

where $\partial/\partial n_s$ denotes differentiation along the normal to s outward from the dispersion medium, s_1 integration around the particle, and $E = -\nabla\psi$. For very thin rods, ϵ remains real until ν becomes almost unity. In such a case, we can expand the hypergeometric functions in the potential (4.5) and neglect the higher order terms of B except the order of $B^{2\epsilon}$. Then we obtain

$$\frac{\delta F_{1(\text{el})}}{\delta a} = \frac{D}{2a} \left(\frac{kT}{e} \right)^2 \{ 2(1 - \epsilon^2) - (1 - \delta^2) + O(B^{2\epsilon}) \}. \quad (4.19)$$

To compare with the pipe model, another rod is also displaced by δa , and in the limit of $b \rightarrow 0$, the result becomes

$$\begin{aligned} - \left(\frac{\partial F}{\partial a} \right)_i &= -2 \left(\frac{\partial F_1}{\partial a} \right) \\ &= \frac{D}{a} \left(\frac{kT}{e} \right)^2 \{ 4\nu - (1 - \delta^2) - 2\nu^2 \}, \quad (\nu \leq 1) \end{aligned} \quad (4.20)$$

$$= \frac{2kT\pi l^2}{a} \{ \bar{C} - C_{(i)} \} - 2 \frac{(Ne)^2}{aD} \quad (4.21)$$

where

$$\bar{C} = \frac{2N}{\pi l^2}. \quad (4.22)$$

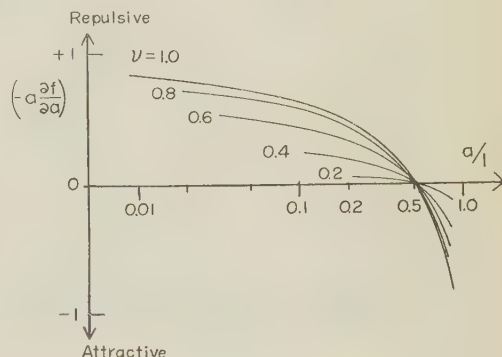


Fig. 5. Numerical results of $\left(-a \frac{\partial f}{\partial a} \right)$ for a/l .

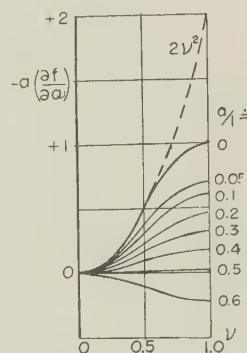


Fig. 6. Numerical results of $\left(-a \frac{\partial f}{\partial a} \right)$ for ν .

By these equations we can calculate the force at various values of charge and distance. Numerical results are shown in Figs. 5, and 6, where a dimensionless quantity f is defined by

$$F = D \left(\frac{kT}{e} \right)^2 f. \quad (4.23)$$

First we see the relation between the force and the distance in Fig. 5. Independently of the charge, the zero point of the force or the minimum point of the free energy is found at

$$a_0 \doteq l/2. \quad (4.24)$$

At this point the densities of counter ions at $r=0$ and $r=l$ are almost the same, as shown in Fig. 7. This result indicates that the equidistant arrangement of rods in the solution is most stable. The stability of this arrangement can be estimated by the average fluctuation of distance defined by

$$\langle (a-a_0)^2/a_0^2 \rangle.$$

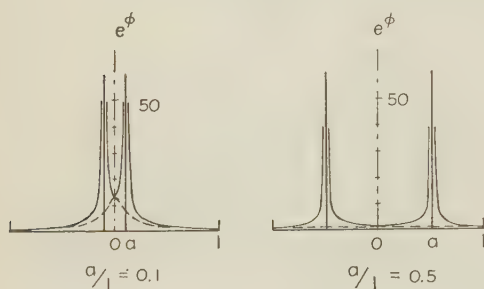


Fig. 7. Counter ion distributions around two rod-like infinitely thin polyelectrolytes for $\nu=1/2$. Solid curves for $\theta=0$ and broken curves for $\theta=\pi/2$.

This quantity is determined from the free energy required for the small displacement of rods from the equilibrium position a_0 . When only the linear fluctuation of distance along the line connecting two rods is allowable, we obtain

$$\langle (a-a_0)^2/a_0^2 \rangle = 1/a_0^2 \left(\frac{\partial^2 (\mathcal{F}/kT)}{\partial a^2} \right)_{a_0}. \quad (4.25)$$

Considering rod-like particles of length h , $\mathcal{F}$ in this equation is given by $\mathcal{F} = Fh = h(D(kT)^2)/e^2 f$. It is easily shown from (4.20) and (4.25) that

$$\langle (a-a_0)^2/a_0^2 \rangle = \frac{e^2}{DkTh} \frac{1}{A} \quad (4.26)$$

where

$$A = a \frac{\partial}{\partial a} \left(a \frac{\partial f}{\partial a} \right). \quad (4.27)$$

It is notable that this A , and therefore the average fluctuation percentage, is a function of charge ν and h , and independent of a_0 or the concentration of rods. The numerical value of A is readily obtained from curves in Fig. 6. For example, when $\nu=1$, $A \approx 1.5$; and when $\nu=0.2$, $A \approx 0.2$. If we consider rod molecules of $h=2 \times 10^{-5}$ cm we have

$$\langle (a-a_0)^2/a_0^2 \rangle \approx \begin{cases} 0.003 & \text{for } \nu=1 \\ 0.02 & \text{for } \nu=0.2. \end{cases} \quad (4.28)$$

As a matter of course, we can find that the fluctuation is decreased with increase in the charge density and also decreased with increase in the size or the total charge number of rods.

The corresponding case of pure Coulomb interaction is given by the fluctuation of a charged rod sandwiched between two parallel rods in a solution containing no counter ions. The average fluctuation of the middle rod along the line connecting two fixed rods is expressed by a formula similar to (4.26) with A equal to $4\nu^2$. Therefore, for example, when $\nu=1$, the fluctuation of rods with counter ions is about twice as large as that of rod without counter ions. However, as compared with the case of no charge where $\langle (a-a_0)^2/a_0^2 \rangle = 1/3$, the electric interaction between rods with counter ions has still a considerably large effect of stabilizing the equidistant arrangement.

Now attention must be paid to the relation between the force and the charge density. Although the force is strengthened with increase of the charge density, the situation is remarkably modified by the condensation of counter ions in the vicinity of rods. The ordinate of Fig. 6 may be regarded as a quantity proportional to the square root of the apparent charge of rods; which is decreased with increasing distance between rods on account of screening of the charge on rods by counter ions around them.

For an infinitely thin rod, it was shown⁹⁾¹⁰⁾ that the counter ion condensation phenomenon always begins to occur at charge $\nu=1$, and when charge ν exceeds unity, the further increase of charge does not bring about the increase of electric potential because the excess counter ions are condensed on the surface of rod. Therefore, in the system of two rods it is interesting to see what will happen if the two infinitely thin rods, each of which has charge $\nu > 1/2$ come to contact and unit into one rod. From (4.11) it follows that when L tends to infinity,

$$\left. \begin{aligned} \delta &= 1-2\nu, & 1/2 \geq \nu \geq 0, \\ \delta &= 0, & 1 \geq \nu \geq 1/2. \end{aligned} \right\} \quad (4.29)$$

In such cases (4.20) can be written as

$$-a \frac{\partial f}{\partial a} = \begin{cases} 2\nu^2 & 1/2 \geq \nu \geq 0 \\ 1-2(1-\nu)^2 & 1 \geq \nu \geq 1/2 \end{cases}. \quad (4.30)$$

It is instructive to compare this result with

the pure Coulomb repulsion between two infinitely thin rods with no counter ions. This pure Coulomb repulsion is proportional to the square of charge $2\nu^2$ as given by the broken curve in Fig. 6. For charge ν smaller than $1/2$, the force between two rods closely approaching in the solution of counter ions coincides with the Coulomb repulsion; which means that in the limit of $L \rightarrow \infty$ no counter ions are fixed to the rods. For charge ν larger than $1/2$, however, even in the limit of $L \rightarrow \infty$, the force between rods is considerably smaller than the Coulomb repulsion. Two rods come into contact, with some of the counter ions in their extreme vicinity. At $\nu=1$, the force between two rods with counter ions becomes just half of the Coulomb repulsion, and corresponds to the swelling force of single infinitely thin rod bearing charge $\nu=1$. On melting of two thin rods of charge $\nu=1$ into one rod (of charge $\nu=2$), the situation in the vicinity of the rods seems to be similar to infinitely thinning of single rod of charge $\nu=1$.

§ 5. General Treatment of Cylindrical Coordinate Systems

In a system of two rods let us divide the the total free energy into two parts, namely,

$$F = F_e + F_m \quad (5.1)$$

where F_e is the electric free energy and F_m is the standard free energy of the non charged system which is given by the ideal mixing entropy of counter ions with the solvent, i.e.,

$$F_m = -2NkT \ln \{\pi(l^2 - 2b^2)\} \quad (5.2)$$

As shown in the previous section, the electric potential is a function of ratios l/a and b/a , and consequently, we can find that the electric free energy is also a function of these ratios. Thus we write

$$F_e = F_e \left(\ln \frac{l}{a}, \ln \frac{b}{a} \right) \quad (5.3)$$

Therefore we can relate the derivative $(\partial F / \partial a)_{i,b}$ which gives the force between two rods to the derivatives $(\partial F / \partial l)_{a,b}$ and $(\partial F / \partial b)_{i,a}$ in the following way.

$$\left(\frac{\partial F}{\partial a} \right)_{i,b} = \left(\frac{\partial F_e}{\partial a} \right)_{i,b} = -\frac{1}{a} \left(\frac{\partial F_e}{\partial \ln(l/a)} \right) - \frac{b}{a} \left(\frac{\partial F_e}{\partial \ln(b/a)} \right) \quad (5.4)$$

$$\left(\frac{\partial F}{\partial l} \right)_{a,b} = \frac{1}{l} \left(\frac{\partial F_e}{\partial \ln(l/a)} \right) - 2kT \frac{2Nl}{l^2 - 2b^2} \quad (5.5)$$

Now, the swelling force of the neutrality zone $(\partial F / \partial V)_{,b}$ is given by the osmotic pressure of counter ions at the circumference because there the electric field is negligible. That is to say,

$$\frac{\partial F}{\partial V} = -kTC_{(i)} \quad (5.6)$$

or

$$\left(\frac{\partial F}{\partial l} \right) = -\frac{2kTV}{l} C_{(i)} \quad (5.7)$$

Combining (5.7) with (5.4) and (5.5), it follows that

$$-\left(\frac{\partial F}{\partial a} \right)_{i,b} = \frac{2kTV}{a} \{\bar{C} - C_{(i)}\} + \frac{b}{a} \frac{\partial F}{\partial b} \quad (5.8)$$

where

$$\bar{C} = \frac{2N}{\pi l^2} \quad (5.9)$$

The second term of (5.8) can be calculated by the general expression of Bell and Levine (2.1), and when $b/a \ll 1$, it is written as

$$\frac{\partial F}{\partial b} = \frac{\partial E_s}{\partial b} \quad (5.10)$$

where E_s is the self energy of two rods, namely

$$\frac{\partial E_s}{\partial b} = -2 \frac{(Ne)^2}{Db} \quad (5.11)$$

Thus we obtain the same result with (4.21). If the total free energy is differentiated by a , under the condition that the ratio b/a remains constant, the second term of (5.8) vanishes and the force between rods is given by the same expression as (3.25) of the pipe model.

To problems of one rod or one pipe also, a similar treatment can be applied. In these cases the electric free energy is a function of the ratio l/b alone, and we can arrive at the result

$$-\left(\frac{\partial F}{\partial b} \right)_i = \frac{2kTV}{b} \{\bar{C} - C_{(i)}\} \quad (5.12)$$

where it is to be noted that the mean density $\bar{C}$ is always given by

$$\bar{C} = (\text{total charges on rod}) / \pi l^2$$

Eq. (5.12) is the same as (3.25). The derivation of force (5.12) is applicable to a rigid rod as well as to a pipe; that is, the swelling force of a rod into which counter ions are not permeable is given by an expression similar to that of a pipe. In a constant cylindrical volume of solvent, the

equilibrium radius of this rod is determined by the condition $\bar{C}=C_l$, and it becomes smaller than the equilibrium radius of a pipe of the same density.

Now, Eqs. (5.8) and (5.12) can be rearranged in the following way

$$\left. \begin{aligned} -a \frac{\partial F}{\partial a} &= 2kTV \{ \bar{C} - C_{(l)} \} + b \frac{\partial F}{\partial b} \\ 0 &= 2kTV' \{ \bar{C}' - C'_{(l)} \} + b' \frac{\partial b_l}{\partial F'} \end{aligned} \right\} \quad (5.13)$$

where the prime refers to the one rod or pipe system. From this result some remarkable conclusions are obtained.

When we consider rods of the same charge density, if b and b' are both sufficiently small, we can put

$$b \frac{\partial F}{\partial b} = 2b' \frac{\partial F'}{\partial b'} \quad (5.14)$$

If, moreover, we put

$$V' = V/2, \quad \bar{C}' = \bar{C} \quad (5.15)$$

the expression of the force between two rods becomes

$$-\frac{\partial F}{\partial a} = \frac{2kTV}{a} \{ C'_{(l)} - C_{(l)} \}. \quad (5.16)$$

This means that the force between two rods is proportional to the difference between the counter ion concentration at the circumference of the free volume of two rods and that of the one rod system; where the free volume of the one rod system is chosen to be half of the two-rod system and the charge per rod is the same. The free energy minimum occurs at

$$C'_{(l)} = C_{(l)}. \quad (5.17)$$

It is readily expected that this condition is satisfied at $a_0 = l/2$, which was indeed confirmed by numerical calculations.

From (5.16), the average fluctuation of distance of (4.25) can be rewritten as

$$\begin{aligned} \left\langle \frac{(a-a_0)^2}{a_0^2} \right\rangle &= \frac{1}{2Va_0 \left(\frac{\partial C_l}{\partial a} \right)_{a_0}} \\ &= \frac{1}{2\mathcal{N}} \frac{1}{a_0 \left(\frac{\partial (C_l/\bar{C})}{\partial a} \right)_{a_0}} \end{aligned} \quad (5.18)$$

where $\mathcal{N} = Nh$ is the total number of counter ions per rod. A relation comparable to this equation can be obtained from the usual one-rod model. In a solution of rod-like polyelectrolytes, if we employ the model of

cylindrical free volume V per rod, the concentration fluctuation or the free volume fluctuation in this solution can be given by

$$\begin{aligned} \left\langle \frac{(V-V_0)^2}{V_0^2} \right\rangle &= \frac{1}{V_0^2 \left(\frac{\partial^2 (\mathcal{F}/kT)}{\partial V^2} \right)_{V_0}} \\ &= \frac{1}{-\mathcal{N} V_0 \left(\frac{\partial (C_l/C)}{\partial V} \right)_{V_0}} \end{aligned} \quad (5.19)$$

considering that V is proportional to a^2 , this relation has a form equivalent to (5.18).

For understanding the behavior of the force between two rods approaching closely, it is useful to transform (5.13) in the following way.

When two rods, each of which has charge ν , approach closely, the concentration $C_{(l)}$ at the circumference of volume V can be approximated by $C'_{(l)}$ at the circumference of free volume $V' = V$ of one rod having charge 2ν . Therefore, we have

$$-a \frac{\partial f}{\partial a} = b \left(\frac{\partial f}{\partial b} \right) - b' \left(\frac{\partial f'}{\partial b'} \right) \quad (5.20)$$

where the first term $b(\partial f/\partial b)$ is given by $-2\nu^2$ when $\nu < 1$ and $b/a \ll 1$. The second term $b'(\partial f'/\partial b')$ which means the swelling force of one rod having charge 2ν is given by

$$b'(\partial f'/\partial b') = 4\nu - (1 - \delta^2) \quad (5.21)$$

where for very thin rod

$$\left. \begin{aligned} \delta &= (1 - 2\nu) & \text{when } 1/2 \geq \nu \geq 0 \\ \delta &= 0 & \text{when } \nu \geq 1/2. \end{aligned} \right\} \quad (5.22)$$

From (5.20) and (5.22) we can derive (4.30). Thus when two rods come into contact, the force between them is given by the difference between the swelling force of a thin rod having charge 2ν and that of two independent thin rods of charge ν , as shown in Fig. 8.

In developing the general theory of force in this section, the relation (5.6) played an important role. This relation is satisfied under the condition that the electric field vanishes at the circumference. For the system of two rods, the field is not always zero at the circumference. When counter ions are absent, the fluctuation of electric potential and electric field is estimated to be

$$|\phi_{(L,\theta)}|_{\max} \sim 0.29, \quad \left| x \frac{\partial \phi}{\partial x} \right|_{\max, x=L} \sim 2.66 \quad (5.23)$$

for $\nu = 1/2$ and $L = 2$. In our system with

counter ions, however, the fluctuation becomes small owing to the strong suppression of the potential by counter ions. For the above values of ν and L we have

$$|\phi_{(L,\theta)}|_{\max} \sim 0.16, \quad \left| x \frac{\partial \phi}{\partial x} \right|_{x=L} \sim 0.55 \quad (5.24)$$

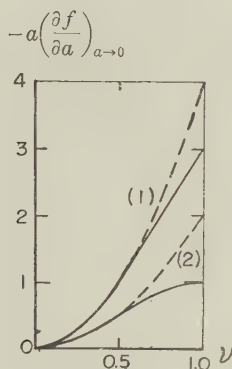


Fig. 8. Effects of counter-ion condensation on the swelling force of one rod and on the repulsion between two rods.

(1) For one rod with charge $\nu=2$.

(2) For two rods with charge $\nu=1$.

(Solid curves: with counter ions. Broken curves: without counter ions.)

In such a case, the error in the expression of force (4.21) or (5.8) caused by the approximation (4.10) or (5.6) does not exceed 10 per cent, because

$$\frac{D}{8\pi} \left\langle \left(\frac{\partial \phi}{\partial r} \right)^2 \right\rangle_{r=l} = \frac{\left\langle \left(x \frac{\partial \phi}{\partial x} \right)^2 \right\rangle_{x=L}}{4(1-\delta^2)} < 0.1. \quad (5.25)$$

In other words, the potential or the field around two rods rapidly becomes of circular symmetry and the settlement of the circular neutrality zone for the two rod system is reasonable as long as the rods do not approach too closely to the outer circumference.

References

- 1) L. Onsager: Ann. N.Y. Acad. Sci. **51** (1949) 627.
- 2) A. Isihara: J. Chem. Phys. **19** (1951) 1142.
- 3) P. J. Flory: Proc. Roy. Soc. A, **234** (1956) 73.
- 4) G. Oster: J. Gen. Physiol. **33** (1950) 445.
- 5) I. Michaeli, J. Th. G. Overbeek and M. J. Voorn: J. Polymer Sci. **23** (1957) 443.
- 6) N. Imai and T. Ohnishi: J. Chem. Phys. **30** (1959) 1115.
- 7) S. Asakura, N. Imai and F. Oosawa: J. Polymer Sci. **13** (1954) 499.
- 8) G. M. Bell and S. Levine: Trans. Faraday Soc. **54** (1958) 785.
- 9) R. M. Fuoss, A. Katchalsky and S. Lifson: Proc. Natl. Acad. Sci. (U.S.) **37** (1951) 579.
S. Lifson and A. Katchalsky: J. Polymer Sci. **13** (1954) 43.
- 10) T. Alfrey, Jr., P. W. Berg and H. Morawetz: J. Polymer Sci. **7** (1951) 543.
- 11) N. Imai and F. Oosawa: Busseiron-Kenkyu, nos. 46, 47 (1952).
- 12) N. Imai (to be published).

Formation of a Plasma by Low Energy Ion Injection and Cyclotron Heating

By Tarô DODO

Hitachi Central Research Laboratory, Kokubunji, Tokyo, Japan

(Received January 6, 1960)

A new method has been devised to produce a high temperature plasma by injecting an ion beam into a static magnetic mirror field.

In this method, ions are injected along the axis of the D.C. magnetic field lines and are given energy through the oscillating electro-magnetic field of the cyclotron frequency. Therefore, the magnetic moments of ions are increased while it travels from one end of the mirror field to the other end. The injected ions are thus reflected at the opposite mirror end and some of them perform reciprocating motions between both ends. While an in-phase ion gets energy from the R.F. field, an out-of-phase ion is decelerated and escapes from the mirror ends. The probability of trapping an injected ion is about three-tenths to one-half, depending on the strength of the oscillating field.

As the ion current becomes large, which is opposite phase to the external R.F. current, the injected ions are no longer trapped. In our device, the ion density will be limited to about $10^{12}/\text{cm}^3$.

§ 1. Introduction

In producing a high temperature plasma, it is highly advantageous to adopt the method of injecting an ion beam from outside of the static magnetic field and confining ions within it, though this method is not so frequently adopted in actual experiments.^{1),2)} Our apparatus is designed so that the ions injected from one end of the magnetic mirror along the magnetic axis may be trapped within the mirror field through gaining kinetic energy perpendicular to the axis from the external R. F. field. That is to say, the velocity of ions, which is initially inside the "loss cone³⁾" of the magnetic mirror, gets out of the loss cone under the influence of the R. F. field,

whose frequency is resonant with the ion gyration.

Our device needs only a high intensity ion source, while in DCX¹⁾ it is necessary to have a special device to dissociate molecular ions efficiently in addition to a high intensity accelerator.

If a uniform magnetic field is used, the ion energy continues to increase until the ions hit the walls of the container and are lost, so that the ion density will be insufficient to produce the "burn-out²⁾" state. When a non-uniform magnetic field is used, an ion injected near the axis of magnetic field gains energy but a high energy ion, which passes through the region far from the axis, does not satisfy the resonance condition. The ion energy, therefore, will not exceed some value E_f . The ion density will then get large and neutral atoms will be "burnt-out".

In the beam injection method, the velocity distribution is like δ -function rather than the Maxwell distribution. In the similar device using this method aiming at the D - D fusion reaction, the rate of fusion reaction $\langle \sigma_f v \rangle$ is greater for the δ -function-like distribution than for the Maxwell distribution provided that the mean energy is greater than 100 keV. The cross section for ionization σ_i reaches the maximum near 200 keV. It is therefore desirable that the ion energy is more than 200 keV

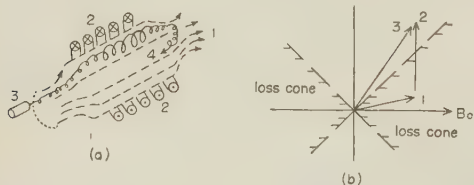


Fig. 1. Schematic drawing of the injection and trapping of ions by cyclotron resonance.

(a) 1: Static magnetic field lines. 2: R.F. coils. 3: Ion source. 4: Orbit of an ion.

(b) 1: Velocity vector of an injected ion. 2: Velocity component given by R.F. field. 3: Resultant velocity vector of an ion after passing through R.F. field.

so long as the thermonuclear fusion device using the beam injection method is concerned.

Besides advantages common to the ion beam injection devices, our device has the advantage that fuel ions alone are supplied with energy and that the ion density of plasma is likely to be higher than the density of injected ions, because the ions produced by ionization also get energy.

The apparent defect of our device, on the other hand, lies in that the ion current shows strong reaction to the external R. F. field. That is to say, when the ion density reaches $10^{12}/\text{cm}^3$, the effect of shielding the external R. F. field becomes strong and the injected ions cease to be trapped any longer. This phenomenon will be discussed in Appendix II.

After we had planned our device, we found that the apparatus "Albedo¹¹⁾" is based on the same principle as ours. However, we were unable to find any detailed report on "Albedo" and the reason why this device had been abandoned.

§ 2. Motion of an Ion in the R. F. Field

In this section, the motion of an ion in the uniform magnetic field will be discussed.

In the z -direction, there exist an uniform magnetic field and the axially symmetric R. F. field which is superimposed on the former. We shall analyse the motion of single ion, moving with the constant velocity in the z -direction, since the collision between ions, whose density is small, is negligible.

In the external field

$$\begin{aligned} \mathbf{B} &= (0, 0, B), \quad B = B_0(1 + \varepsilon \sin \omega t), \\ \mathbf{A} &= (-y, x, 0)(B/2), \end{aligned} \quad (1)$$

the equations of motion of an ion are

$$\ddot{\xi} = -i[(\dot{\omega}_c/2)\xi + \omega_c \dot{\xi}], \quad (2)$$

$$\xi = x + iy, \quad (3)$$

$$\omega_c = eB/mc = \omega_0(1 + \varepsilon \sin \omega t) \quad (3)$$

$$\left. \begin{aligned} \ddot{r} - r\dot{\theta}^2 - \omega_c r\dot{\theta} &= 0, \\ \frac{\alpha}{dt} \left(r^2\dot{\theta} + \frac{1}{2}\omega_c r^2 \right) &= 0. \end{aligned} \right\} \quad (4)$$

The gyration radius of the ion is supposed to be sufficiently small compared with the distance ξ_0 between the central axis of the magnetic field and the guiding center of the ion orbit. Expanding ξ into a power series of ε , we solve Eq. (2) by the perturbation method.

$$\xi = \xi_0 + \xi_1(t) + \xi_2(t) + \dots \quad (5)$$

$$\xi_0: \text{constant}, \quad \xi_1: \text{order of } \varepsilon,$$

$$\xi_2: \text{order of } \varepsilon^2, \dots$$

The first order equation with regard to ε is

$$\ddot{\xi} + i\omega_0 \xi_1 = -i\alpha \xi_0 \cos \omega t, \quad \alpha = \varepsilon \omega \omega_0/2. \quad (6)$$

The particular solution of this equation is

$$\xi_1(\varepsilon) = -i(\alpha \xi_0/\omega) \int \exp[-i\omega_0(t-t')] \sin \omega t' dt' \quad (7)$$

In case of $\omega = \omega_0$ and $t \gg 1/\omega$, the oscillating term can be neglected, and the above expression becomes

$$\xi_1(\varepsilon) = (\alpha \xi_0 t/2\omega) \exp[-i\omega t]. \quad (8)^*$$

Let l be the axial length of the R. F. field. Let the initial velocity of the ion perpendicular $\mathbf{B}_0$ field be v_0 and the velocity in z -direction be w_z . When the phase difference between R. F. field and the gyratory motion of the ion at the entrance of the R. F. heating section is β , the velocity v_1 of the ion when it reaches the other end of the mirror field can be represented as follows:

$$\begin{aligned} v_1 &= (\alpha \xi_0/2)(l/w_z) \exp[-i\omega t] \\ &+ v_0 \exp[-i\omega t] \exp[i\beta]. \end{aligned} \quad (9)$$

And the energy of the ion after passing through the R. F. field is

$$\begin{aligned} (m/2)|v_1|^2 &= (m/2)[(\alpha \xi_0/2)^2(l/w_z)^2 \\ &+ \alpha \xi_0 v_0(l/w_z) \cos \beta + v_0^2]. \end{aligned} \quad (10)$$

In this equation, the first term on the right hand side represents the energy gain E_1 which an ion obtains on the average when it passes through the R. F. heating section. The condition under which the ion is reflected on the mirror field $\mathbf{B}_1$ is

$$w_z^2 + |v_1|^2 - (B_1/B_0)|v_1|^2 \leq 0. \quad (11)$$

* If we use a new variable η ,

$$\eta = \xi \exp \left[(i/2) \int \omega_c(\tau) d\tau \right],$$

Eq. (2) becomes to Hill's equation

$$\ddot{\eta} + (\omega_c^2/4)\eta = 0.$$

From the first order solution of this equation by the standard method,¹²⁾ we get ξ as a linear combination of

$$1, \{1 - i \exp(-i\omega t) + (\varepsilon/8) \exp(i\omega t)\} \exp(\varepsilon \omega t/4),$$

$$\text{and } [1 + i \exp(-i\omega t) + (\varepsilon/8) \exp(i\omega t)] \exp(\varepsilon \omega t/4).$$

If we take the first order term of the power series expansion of $\exp(\varepsilon \omega t/4)$, we get the same solution as expression (8).

The intensity ϵ of the R. F. field needs to satisfy the following inequality in order that the ion can be reflected from the mirror field B_1 even when the initial velocity and the R. F. field are in the most unfavorable phase relation (i.e. $\cos \beta = -1$ in equation (12))

$$w_z^2 \leq (M-1)[(\alpha \xi_0/2)(l/w_z) - v_0]^2, \\ M = B_1/B_0 = \text{mirror ratio.} \quad (12)$$

§ 3. Experimental Aspects

In this section we explain the outline of a preliminary experiment in progress to test the idea of trapping ions in the magnetic mirror field.

(1) Apparatus

The metal vessel (inner dia.: 20 cm, length: 600 cm) serves to shield the electromagnetic coupling between R. F. coils and coils for D. C. magnetic field. The vacuum chamber has an inner diameter of 10 cm, a length of 400 cm and is made of quartz glass.

There is a uniform magnetic field with strength of 10^4 gauss over the length of 220 cm. The strength of magnetic mirrors on both sides of the uniform field is 2×10^4 gauss.

Deuterium ions are produced through low voltage arc discharge. Ions are injected at 400 eV. The lower the energy of injection, the more favorable in our apparatus. However, the lower limit of energy at which ions may be extracted stably is about 400 eV. The ion source of Caltron type is placed in the position of 2×10^4 gauss. The electron gun is placed at the mirror and opposite to the ion source.

To satisfy the condition (12) and to trap injected ions in the magnetic bottle, the R. F. oscillator will need the power of about 20 kW assuming the Q -value of the coil system to be 100. The necessary power of oscillator to trap ions in the mirror field will be proportional to the square of the injection energy.

(2) Injection and escape of ions from mirror ends

If power is supplied to the R. F. oscillator to such an extent that the inequality (12) may be satisfied, ions which have been injected from one end (X -end) of the mirror will all be reflected from the other end (Y -end).

However, some of them reflected at Y -end may reenter the R. F. heating section out of phase and their magnetic moments decrease,

then they escape from the X -end. If the equality in the expression (12) is satisfied, one-third of injected ions are estimated to escape from the X -end at the second reflection. The mean energy of ions reflected at the X -end is greater than that of ions of the preceding reflection at the Y -end. Accordingly, at the third reflection one-ninth of them will escape from the Y -end. In consequence of repeated reflections about seven-tenths of injected ions will escape from the magnetic mirror field. A detailed calculation concerning the escape probability of an ion is given in Appendix I.

(3) Energy and density of ions

An ion, injected from the ion source, gains an energy E_1 on the average on its every passage through the heating section. Therefore, the radius of its gyrotory motion will gradually increase. When the radius ρ_0 of ionic orbit becomes about half of radius R_0 of the container, the ionic orbit contacts the walls of the container, and high energy ions will be lost. The maximum energy $E_{\max}$ of an ion confined in the container is, therefore, determined by

$$\rho_0 = c\sqrt{2mE_{\max}}/eB_0 \cong R_0/2. \quad (13)$$

As described in Appendix III, the guiding center of gyration drifts outside due to the conservation law of generalized angular momentum.

The ion density n_i is determined as follows:

$$n_i = (I_+/V)\tau_0 P, \quad (14)$$

where I_+ is the injected ion current, V is the plasma volume, $\tau_0 = (E_{\max}/E_1)(l/w_z)$ is the time in which the ion energy reaches $E_{\max}$ after being injected and P is the probability that ions are trapped.

The charge exchange collision rate $R_{ex} = n_i n_0 \sigma_{ex} v$ and the ion-ion collision rate $R_{coll} = (1/2)n_i^2 \sigma_e v$ are, in our apparatus, very small compared with the injection rate $R_{in} = (I_+/V)P$. Therefore, the ion density has nearly the same value as that given by the Eq. (14).

The energy spectrum of ions is obtained from the numerical solution of integral equation and Monte Carlo method. The method of calculation is described in Appendix IV.

Neutral atoms are removed by the charge exchange collision or ionization. However, the removal rate by these processes is, in our case, very small compared with the

flowing rate $R_{flow} = (n_0 v_0 S / 4V)$, where v_0 is the average velocity of neutral atoms and S is the plasma surface area. Therefore, there will be almost no decrease in the total number of neutral atoms, i.e. a "burnt-out²⁾" state will not be realized in our apparatus.

With regard to our apparatus, numerical values of the above parameters are as follows: $B_0 = 10^4$ gauss, $I_+ = 200$ mA $= 1.2 \times 10^{18}$ ions/sec, $E_1 = 400$ eV, $P \approx 1/2$, $R_0 = 5$ cm, $V = 1.6 \times 10^4$ cm³, $S = 6 \times 10^3$ cm², $n_0 = 7 \times 10^9$ cm⁻³ (neutral gas pressure 10^{-7} mmHg);

$E_{max} \approx 20$ keV, mean energy ≈ 5 keV (cf. Fig. 2), $\tau_0 \approx 5 \times 10^{-4}$ sec, $n_i \approx 2 \times 10^{10}$ cm⁻³, $\sigma_{ex}^{(4)} \approx 4 \times 10^{-16}$ cm², $\sigma_o^{(5)} \approx 10^{-19}$ cm², $\sigma_i^{(9)} < 10^{-16}$ cm², $v \approx 7 \times 10^7$ cm/sec, $R_{in} \approx 3.8 \times 10^{13}$ /sec cm³, $R_{ex} \approx 4 \times 10^{12}$ /sec cm³, $R_{coll} \approx 1.5 \times 10^9$ /sec cm³, $R_{flow} = 8.5 \times 10^{13}$ /sec cm³.

R_{ex} and R_{coll} are computed for simplicity on the assumption that all ions have the same energy 5 keV.

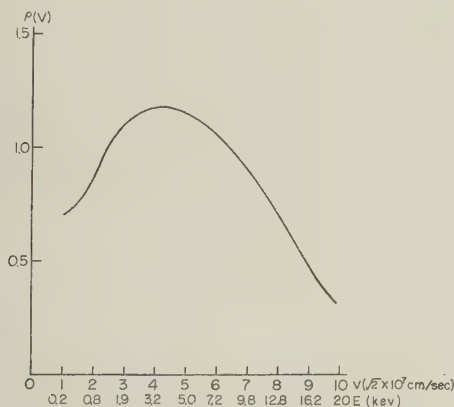


Fig. 2. Energy spectrum of ions computed by the numerical solution of integral equation.

By ionizing residual neutral atoms, electrons can be supplied, so it may be almost unnecessary to install an electron gun. In a large apparatus in which high energy ions with an energy of about 250 keV can be confined, as described in § 4, σ_i increases; therefore, it is quite unnecessary to install an electron gun.

The mean energy of electrons can be obtained by calculating how much energy the electrons, put into the ions having an energy spectrum as shown in Fig. 2, will gain until they are lost from the mirror field. Here in this paper, however, a more rough estimate was made. That is to say, the electrom temperature was obtained through the following

equation, which is valid for ions in case of the Maxwell distribution at T_i ,

$$\frac{dT_e}{dt} = \frac{8\sqrt{2}\pi}{3} (\log A) \frac{n_e e^4}{(kT_e)^{3/2}} \frac{m^{1/2}}{M} T_i, \quad (15)^7$$

where m and M are electron and deuteron masses, respectively, $A = (\text{the Debye shielding length}) / (\text{the distance of closest approach})$, and k is the Boltzman constant. If electrons are injected in the same number as that of ions, then the mean life of electrons is about 5×10^{-4} sec, or the same as that of ions. When the mean energy of ions is 5 keV, that of electron will be 25 eV. Even when electrons are supplied through ionization of residual neutral gases . . . accordingly, even if it is supposed that the mean life of electrons is very long (~ 1 sec.) . . . , the electron energy will amount to only several hundred eV.

§ 4. An Approach to Thermonuclear Plasma

To avoid the defect of the preliminary experimental apparatus, a device using a non-uniform static field is planned.

In this device, ions will not be accelerated above an energy E_f (cf. Appendix III). The ion density is determined by the two following factors:

- (1) The external R. F. field is shielded by ion currents. Therefore, the injected ions become hard to be trapped.
- (2) The trapped ions are lost as results of ion-ion collision and charge exchange collision.

The process (1) peculiar to our device is an important factor determining the upper limit of the ion density. The ion current in plasma, with the opposite phase to the external R. F. current, weakens the externally induced field in plasma. As is shown in Appendix II, when the ion density grows up to the critical value n_{crit} the induced field-strength in plasma becomes about half of that in absence of ions. Therefore, the injected ions are unable to get sufficient energy to be reflected at the mirror end.

Accordingly, the ion density in this device is limited to about n_{crit} . From Fig. 5 in Appendix IV, it may be regarded that the energy spectrum of ions concentrates near E_f .

In this device, E_f may be a few hundred keV. So the ionization rate becomes large and the removal rate $R_{rem} = n_0 n_{crit} (\sigma_{ex}^{(8)} + \sigma_i^{(9)}) v$ of neutral atoms becomes greater than the

flowing rate R_{flow} . Therefore, fully ionized plasma state will be realized.

An example for this device is:

$R_0=25$ cm, $V=1.4 \times 10^5$ cm³, $S=1.5 \times 10^4$ cm²,
 $n_0 = 7 \times 10^9$ /cm³, static field $H_z = H_0 + H_2 I_0(\kappa r) \sin \kappa z$, $H_0=10^4$ gauss, $H_2=950$ gauss,
 $2\pi/\kappa=35$ cm;

$E_f \simeq 250$ keV, $n_{crit} \simeq 10^{12}$ /cm³, $R_{coil} = 1 \times 10^{10}$ /sec cm³, $R_{ez}=1.4 \times 10^{13}$ /sec cm³, $R_{rem}=3.3 \times 10^{14}$ /sec cm³, $R_{flow}=2.5 \times 10^{13}$ /sec cm³.

R_{coil} , R_{ez} and R_{rem} are computed assuming the ion energy to be 250 kV.* To get the "burn-out", the injection current will need to be 100 mA when the trapping probability P is assumed to be 1/2. Neutral atoms will be ionized near the plasma surface, because the effective mean free path λ of a neutral atom in the plasma is given by

$$\lambda = v_0 / [n_{crit}(\sigma_{ex} + \sigma_i)v],$$

and is about 3 cm in our case. The ions, produced by ionization of neutral atoms, are larger in number than those injected from the ion source.

The ions produced by ionization of neutral atoms have small w_z . Hence, they are trapped in the mirror field even if the strength of the oscillating magnetic field is weak. Therefore, there is a possibility that the ion density will be greater than n_{crit} .

Dividing the electron density 10^{12} /cm³ ($\sim n_{crit}$) by their supplying rate $R_{ionization} \simeq R_{flow}$ **, we get 10^{-1} sec as the order of the mean life of electrons remaining in the plasma region. Taking their mean life as 10^{-1} sec and by use of eq. (15), we get 5 keV as the mean energy of electrons. Since the collision time of

* The charge exchange cross section decreases sharply with deuteron energy above 70 keV. The mean time between charge exchange collisions in the range of 0.4 keV to 70 keV is

$$(n_0 \sigma_{ex} v)^{-1} \simeq 4 \text{ m sec.}$$

On the other hand, the average time of injected ions getting energy upto 70 keV is

$$(70 \text{ keV}/400 \text{ eV})(l/w_z) \simeq 0.6 \text{ m sec.}$$

$$(l \simeq 70 \text{ cm}; w_z \simeq 2 \cdot 10^7 \text{ cm/sec}).$$

Since, it can be regarded that the energy of almost all ions comes upto 250 keV (σ_e is far smaller than σ_{ex}).

** Because $\sigma_i \gg \sigma_{ex}$, most neutral atoms are ionized.

electrons is very short***, some of electrons escape rapidly from the plasma region. Therefore, the plasma will be positively charged to the order of mean kinetic energy of electrons and remaining electrons will be trapped by this electrical potential.

Acknowledgements

The author wishes to express his sincere thanks to Dr. T. Ohkawa of Tokyo University for his valuable advices and discussions, who had a similar idea as described in this paper. He is also grateful to Dr. S. Nagao of Tohoku University, Prof. K. Husimi of Osaka University and Dr. B. Tadano of our laboratory for their constant encouragements and discussions. He is indebted to Messrs. K. Matsuo and T. Kawai for their helps in the calculations and discussions. He is obliged to Mr. M. Tanaka of Japan Atomic Research Institute for his valuable suggestions.

Appendix I. Escape Probability of Ions from the Mirror Ends

As for the injection of ions from the ion source placed at an mirror end, there are two extreme cases, i.e., one (Case I) in which ions are injected in parallel to the magnetic field B_0 and the other (Case II) in which ions are injected with their velocities in the direction of B_0 almost zero. In Case II, with a slight acceleration of ions their velocity vectors come outside the loss cone. With a very small power of the R. F. oscillator, therefore, half of the injected ions can be reflected at the other mirror end. However, in order to reflect all of ions having arbitrary phase relations with the oscillating magnetic field, it is necessary to have the oscillating magnetic field of the same order of magnitude as in Case I.

The strength ϵ of the oscillating magnetic field, which is necessary to reflect at the Y-end all ions injected with energy of $(1/2)mu_0^2$, can be determined by the following conditions according to the inequality (12).

$$\text{Case I: } \frac{\alpha \tilde{\epsilon}_0}{2} \frac{l}{u_0} \geq \frac{u_0}{\sqrt{M-1}}, \quad \alpha = \epsilon \omega^2/2, \quad w_z = u_0. \quad (\text{A. I. 1})$$

$$\text{Case II: } u_0^2 = Mv_0^2 = w_z^2 + v_0^2, \\ w_z = \sqrt{(M-1)/M} u_0,$$

*** The collision time of electrons with 5 keV is several milliseconds.

$$\left[\frac{\alpha \xi_0}{2} \sqrt{\frac{M}{M-1}} \frac{l}{u_0} - \frac{1}{\sqrt{M}} u_0 \right] \sqrt{M-1} \\ \geq \sqrt{\frac{M-1}{M}} u_0, \text{ or } \frac{\alpha \xi_0}{2} \frac{l}{u_0} \geq \sqrt{\frac{M-1}{M}} 2u_0. \quad (\text{A. I. 2})$$

In case of $M=2$, ϵ satisfying (A. I. 1) and that satisfying (A. I. 2) have the same value.

The probability of ions, reflected at the Y-end, escaping from the X-end will be computed in case of $M=2$. The strength of the R. F. field will be selected so that the equality of (12) is satisfied.

Case I: All ions, reflected for the first time at the Y-end, enter the R. F. field with the initial velocity $v_0^{(1)}=u_0$ perpendicular to B_0 . Let the phase difference between the gyrotory motion of the ion and R. F. oscillation be β_1 . The velocity $v_0^{(2)}$ of the ion perpendicular to B_0 , when it reaches the X-end, can be expressed as follows from the equation (10):

$$v_0^{(2)}=u_0 \sqrt{2(1+\cos \beta_1)}. \quad (\text{A. I. 3})$$

If $v_0^{(2)}>u_0$, the ion can be reflected. Hence, the ion whose phase difference is $-(2/3)\pi < \beta_1 < (2/3)\pi$ can be reflected at the X-end. Since the phase difference is random between $-\pi$ and π , the probability of an ion escaping from

the mirror end at the second reflection is one-third.

The velocity $v_0^{(3)}$ at the third reflection is

$$v_0^{(3)}=\sqrt{(v_0^{(2)})^2+u_0^2+2u_0v_0^{(2)}\cos \beta_2}. \quad (\text{A. I. 4})$$

In order to satisfy $v_0^{(3)}>u_0$, it is necessary that $|\beta_2|<\cos^{-1}(-v_0^{(2)}/2u_0)=\beta_2'$. Accordingly, the escape probability at the third reflection is derived by

$$(\pi-\beta_2')/\pi=\beta''/\pi=[\cos^{-1}(v_0^{(2)}/2u_0)]/\pi.$$

As for $v_0^{(2)}$, its value depends on the phase difference β_1 . Therefore, in order to obtain the escape probability, $v_0^{(2)}$ should be averaged with respect to β_1 ,

$$\bar{\beta}''=\frac{3}{2\pi}\int_0^{2\pi/3}\cos^{-1}\left(\frac{v_0^{(2)}}{2u_0}\right)d\beta_1 \\ =\frac{3}{2\pi}\int_0^{2\pi/3}\cos^{-1}\frac{\sqrt{2(1+\cos \beta_1)}}{2}d\beta_1=\frac{3}{2\pi}\left(\frac{\pi}{3}\right)^2.$$

The escape probability at the third reflection is

$$(\beta''/\pi)(2/3)=1/9.$$

At the fourth reflection the escape probability is expressed as follows:

$$\frac{3}{\pi^2}\int_1^2\frac{dx}{[4-x^2\cos^{-1}(x/2)]^{1/2}} \\ \times \int_{\cos^{-1}[(3-x^2)/2\pi]}^{\cos^{-1}(-x/2)}\cos^{-1}\frac{(x^2+1+2x\cos \theta)^{1/2}}{2}d\theta.$$

Table 1. Escape probability at each reflection in Case I computed by Monte Carlo method. (No. of tested: 3800)

No. of reflection	1	2	3	4	5	6	7	8	9	10	11
No. of escapes	1300	394	229	138	82	87	69	44	41	30	29
%	34	10	6	4	2	2	2	1	0.8	0.8	0.8
No. of reflection	12	13	14	15	16	17	18	19	20	21	trapped
No. of escapes	26	16	18	18	18	17	15	8	13	9	1119
%	0.7	0.4	0.5	0.5	0.5	0.4	0.4	0.2	0.3	0.2	29%

It is tedious and troublesome to compute analytically the escape probability at the further reflections. From the result computed through the Monte Carlo method,* it is expected that about three-tenths of the injected ions will be trapped in the mirror field.

On the every passage through the heating section, their energy perpendicular to B_0 in-

creases on the average. Since the energy parallel to B_0 is constant, the escape probability decreases as the number of reflections increases.

Case II: All ions are reflected at the first reflection. By the similar computation with Case I, the escape probability at the second reflection is

$$\frac{1}{\pi^2}\int_0^\pi\frac{2+\cos \beta}{(5+4\cos \beta)^{1/2}}d\beta\div 0.1.$$

* Computation in the Monte Carlo method is described in Appendix IV.

It is rather troublesome to compute the escape probability at the third reflection, in this case. The total number of escapes after ten times of reflections will be less than four-tenths of the injected ions.

Appendix II. Reaction of Ion Current to External Oscillating Field

The electromagnetic field is shielded by an current flowing on the plasma surface. By this shielding effect, the intensity of the oscillating electric field in the interior of the plasma is inversely proportional to the ion density when the latter exceeds some limiting value.

On the problems of the shielding effect, T. H. Stix¹⁰⁾ made an extensive discussion. However, concerning the beam injection we shall make a computation to clarify these problems. According to Stix, if the phase of oscillating electric field is changed periodically in the axial direction, then the shielding effect due to the ion current will be diminished on account of an electron current in the axial direction. Therefore, we shall make our calculation on the basis of this configuration.

The mean velocity of ions is expressed as a function of the electromagnetic field, solving the equation of their motion. Substituting the ion current obtained from the mean velocity of ions for the current in Maxwell's equation, we have a homogeneous equation in the electric field alone. Then we have the order of magnitude of the reaction to the external field.

We neglect the electron inertia, so the electric field in the axial direction is assumed to be zero. The axial static field B_0 and the axial velocity w_z of the ion are taken to be zero-order quantities, and the R. F. fields $\mathbf{E}$ and $\mathbf{B}$ and the transverse ion velocity $\mathbf{u}$ are assumed to be first-order quantities. Then the first-order equation of motion is

$$\frac{\partial \mathbf{u}}{\partial t} + w_z \frac{\partial \mathbf{u}}{\partial z} = \frac{Ze}{mc} [\mathbf{E} + \mathbf{u} \times \mathbf{B}_0 + \mathbf{w}_z \times \mathbf{B}] . \quad (\text{A. II. 1})$$

Rewriting this equation with the use of the following expressions

$$u_+ \equiv u_z + iu_y, \quad E_+ \equiv E_z + iE_y, \quad \text{etc.} \quad (\text{A. II. 2})$$

we get

$$\frac{\partial u_+}{\partial t} + w_z \frac{\partial u_+}{\partial z} + i\omega_c u_+ = \frac{Ze}{mc} [E_+ + iB_+],$$

$$\omega_c = ZeB_0/mc. \quad (\text{A. II. 3})$$

If we eliminate B_+ from (A. II. 3) using the Maxwell equation and rewrite

$$E_+ = [\varepsilon_+ \exp(i\omega t) + \varepsilon_- \exp(-i\omega t)] \sin kz, \quad (\text{A. II. 4})$$

then solve the equation (A. II. 3) under the initial condition of $u_+ = 0$ at $t = 0$, we obtain

$$\begin{aligned} u_+ = & (i\omega_c/\omega B_0) \{ [C_+ \varepsilon_+ \exp(i\omega t) \\ & + C_- \varepsilon_- \exp(-i\omega t)] \sin kz + i \{ D_+ \varepsilon_+ \exp(i\omega t) \\ & + D_- \varepsilon_- \exp(-i\omega t) \} \cos kz \} . \end{aligned} \quad (\text{A. II. 5})$$

If the axial velocity distribution function $f(w_z)$, corresponding to beam injection, is given as follows:

$$\begin{aligned} f(w_z) = & \frac{1}{2\alpha\sqrt{\pi}} \left[\exp \left\{ -\left(\frac{w_z - w_{z0}}{\alpha} \right)^2 \right\} \right. \\ & \left. + \exp \left\{ -\left(\frac{w_z + w_{z0}}{\alpha} \right)^2 \right\} \right] , \end{aligned} \quad (\text{A. II. 6})^*$$

the mean transverse velocity $\bar{u}_+$ for $t \gg 1/\omega$ is

$$\begin{aligned} \bar{u}_+ = & -(i\omega_c/\omega B_0) [\bar{C}_+ \varepsilon_+ \exp(i\omega t) \\ & - \bar{C}_- \varepsilon_- \exp(-i\omega t)] \sin kz, \end{aligned} \quad (\text{A. II. 7})^{**}$$

where

$$\bar{C}_{\pm} = 1 + {}_1P_{\pm} + {}_2P_{\pm} + {}_1A_{\pm} + {}_2A_{\pm}, \quad (\text{A. II. 8})$$

$$\left. \begin{aligned} {}_1P_{\pm} = & (\omega_c/\alpha k) \exp \{ -(jq_{\pm})^2 \} \\ & \times \int_0^{jq_{\pm}} \exp(\xi^2) d\xi, \\ {}_1A_{\pm} = & (-i\omega_c/\alpha k) (\sqrt{\pi}/2) \exp \{ -(jq_{\pm})^2 \}, \\ {}_1q_{\pm} = & (kw_z \mp \omega - \omega_c)/\alpha k, \\ {}_2q_{\pm} = & (-kw_z \mp \omega - \omega_c)/\alpha k. \end{aligned} \right\} \quad (\text{A. II. 9})$$

Substituting the ion current $J = (Ze/c)n_i\bar{u}_+$ into the Maxwell equation,^{***} and after some calculations we have

$$\begin{aligned} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \kappa^2 \right) \varepsilon_+^* - \left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right)^2 \varepsilon_- = 0, \\ - \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right)^2 \varepsilon_+^* + \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \nu^2 \right) \varepsilon_- = 0, \end{aligned} \quad (\text{A. II. 10})$$

* The Maxwell distribution can be obtained by setting up the following expressions:

$$w_{z0} = 0, \quad \alpha^2 = 2kT_i/m.$$

** This expression is obtained by using the following equations:

$$\lim_{t \rightarrow \infty} [1 - \exp(-itx)]/x = \delta_+(x) = \mathcal{P}/x + i\pi\delta(x),$$

where $\mathcal{P}$ means a principal value.

*** In the present case, the drift velocity ε/B_0 is about 10^5 cm/sec, whereas $\bar{u}_+ \sim 10^7$ cm/sec. Hence, the electron current due to the drift motion can be neglected.

where

$$\begin{aligned}\kappa^2 &= -2[k^2 - \omega^2/c^2 + (4\pi n_i Z e \omega_c) \bar{C}_+^* / c B^0], \\ \nu^2 &= -2[k^2 - \omega^2/c^2 + (4\pi n_i Z e \omega_c) \bar{C}_- / c B_0] \\ &= -2k^2[1 - \omega^2/c^2 k^2 + 4\pi n_i (Z e)^2 \bar{C}_- / mc^2 k^2],\end{aligned}\quad (\text{A. II. 11})$$

and ε_+^* and $\bar{C}_+^*$ are complex conjugates to ε_+ and $\bar{C}_+$, respectively.

By use of cylindrical coordinates

$$\begin{aligned}E_r + iE_\theta &= [\varepsilon_+' \exp(i\omega t) + \varepsilon_-' \exp(-i\omega t)] \sin kz, \\ \varepsilon_+' &= \varepsilon_+ \exp(-i\theta), \quad \varepsilon_-' = \varepsilon_- \exp(-i\theta)\end{aligned}\quad (\text{A. II. 12})$$

and with the assumption that ε_+' and ε_-' are independent of θ , the equations (A. II. 10) give

$$\left[\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + \frac{\kappa^2 \nu^2}{\kappa^2 + \nu^2} - \frac{1}{r^2} \right] \varepsilon_+'^* = 0, \quad (\text{A. II. 13})$$

$$\varepsilon_-' = -(\kappa^2/\nu^2) \varepsilon_+'^*. \quad (\text{A. II. 14})$$

So long as the ion density is not excessively large, we have

$$|\beta \bar{C}_+^*| \ll 1, \quad \beta \approx 4\pi n_i (Z e)^2 / mc^2 k^2. \quad (\text{A. II. 15})$$

$\varepsilon_+'^*$ is nearly equal to the amplitude of the vacuum field. Since $|C_-| > |C_+|$, we have $|\varepsilon_-| < |\varepsilon_+|$. This indicates that the circularly polarized electric field having the same polarity as the motion of ions is shielded by the ion current. When $|\nu^2| \gg |\kappa^2| (|\beta \bar{C}_-| \gg 1)$, the electric field imparting energies to ions becomes extremely weak. As a result, it will be unable to trap ions in the mirror field.

The order of magnitude of ion density in which injected ions will not be trapped is determined by

$$\beta \bar{C}_- \sim 1. \quad (\text{A. II. 16})$$

Since $\bar{C}_- \sim (\omega_c / \alpha k) (\sqrt{\pi} / 2)$, (A. II, 16) can be rearranged as follows:

$$n_{\text{crit}} \sim \frac{mc^2 k^2}{4\pi (Z e)^2} \left(\frac{\omega_c}{\alpha k} \frac{\sqrt{\pi}}{2} \right)^{-1} = 1.5 \times 10^{13} \frac{A^3 \alpha}{Z^3 B_0 \lambda^3}, \quad (\text{A. II. 17})$$

where A is a mass number and λ is the axial wave length of R. F. coils.

In the device described in § 4 ($B_0 = 10^4$ gauss, $w_z = 2 \times 10^7$ cm/sec, diameter of R. F. coil $\simeq$ diameter of vacuum chamber = 50 cm), we have $\alpha \simeq w_z$ and $\lambda \simeq$ diameter of R. F. coils. Hence,

$$n_{\text{crit}} \sim 10^{12} / \text{cm}^3. \quad (\text{A. II. 18})$$

For the ion satisfying the condition of cyclotron resonance $\omega_c = \omega - kw_z$, (A. II. 5) coincides the expression (8) in § 2. In case of the cyclotron resonance, for $t \gg 1/\omega$, $C_+ \rightarrow 0$

and $D_+ \rightarrow 0$, and

$$C_- = -\omega_c i t / 2, \quad D_- = \omega_c i t / 2.$$

Thus, we have

$$u_+ = (i\omega_c / \omega B_0) (\omega_c / 2) \varepsilon_- t \exp[-i(\omega t - kz)]. \quad (\text{A. II. 5'})$$

Viewing in the coordinate system moving together with ions, we have $z = w_z t$. So the ion moves with the gyrotory frequency $\omega - kw_z = \omega_c$ and (A. II, 5') is exactly the same as (8) in § 2.

The input energy to ions per unit time is

$$\frac{d}{dt} \left(n_i \frac{1}{2} m |\bar{u}_-|^2 \right) = \frac{1}{2} n_i m \left\{ \left(\frac{\omega_c}{\omega} \right)^2 \left| \frac{\varepsilon_-}{B_0} \right|^2 \frac{\sqrt{\pi}}{2} \frac{\omega_c^2}{\alpha k} \right\}. \quad (\text{A. II. 19})^*$$

Since the right hand side is proportional to $|\beta \bar{C}_-| |\varepsilon_-|^2 \propto |\beta \bar{C}_-| |1 + \beta \bar{C}_-|^{-2}$, input energy to ions comes to a maximum when $\beta \bar{C}_- \sim 1$.

For $|q| \gg 1$, as can be seen from equations (A. II. 8), (A. II. 9), and (A. II. 10), the phase difference between the ion current and the external oscillating field becomes $\pi/2$. In this case the cyclotron wave¹⁰⁾ is excited.

Appendix III. Method of Breaking the Resonance Condition when Ion Orbit becomes too Large

As the energy of an ion increases, the guiding centre of its circular orbit drifts outwards. This can be seen from the following conservation law of generalized angular momentum (cf. eq. (4) in § 2):

$$r^2(\dot{\theta} + \omega_c/2) = \text{constant}. \quad (\text{A. III. 1})$$

The fact that $r = \text{constant}$ at $\dot{\theta} = 0$ means that the length of tangent from the origin to the ion orbit is constant.

Now the high energy ion with its guiding centre at large radial distance can be made to gain no energy from the R. F. field by changing the strength of static field in the radial direction.

The axially symmetric magnetic field possessing the above mentioned property would satisfy the Maxwell equations $\nabla^2 \mathbf{H} = 0$, $\text{div } \mathbf{H} = 0$, $\text{rot } \mathbf{H} = 0$, if it is represented as

$$\left. \begin{aligned} H_z &= H_0 + H_2 I_0(\kappa r) \sin \kappa z, \\ H_r &= -H_2 I_1(\kappa r) \cos \kappa z, \end{aligned} \right\} r < R_0 \quad (\text{A. III. 2})$$

* This result can be obtained from the following equation:

$$\lim_{t \rightarrow \infty} \int \left| \frac{1 - \exp(-itx)}{x} \right|^2 dx = 2\pi t \int \delta(x) dx.$$

$$\left. \begin{aligned} H_z &= H'_2 K_0(\kappa r) \sin \kappa z, \\ H_r &= -H'_2 K_1(\kappa r) \cos \kappa z, \end{aligned} \right\} r > R_0 \quad (\text{A. III. 3})$$

where I_0 and K_0 are zeroth-order modified Bessel functions, H_2 and H'_2 are constants determined by the boundary conditions at $r=R_0$, and R_0 is the radius of coils of the static field. The frequency ω of R. F. field is chosen as $\omega = eH_0/mc$.

Ions are injected at a radial distance r_1 of the order of $\kappa r_1 \sim 1$. The constant H_2 is chosen so that the phase difference between the gyration of the injected ion and the R. F. field may increase by π while it traverses from $z=0$ to $z=\pi/\kappa$.* When a high energy ion passes at a radial distance of about $\kappa r_2 \sim 2$, the phase difference between the ion gyration and the R. F. field will increase by 2π while it traverses from $z=0$ to $z=\pi/\kappa$. (see Fig. 3 (a))

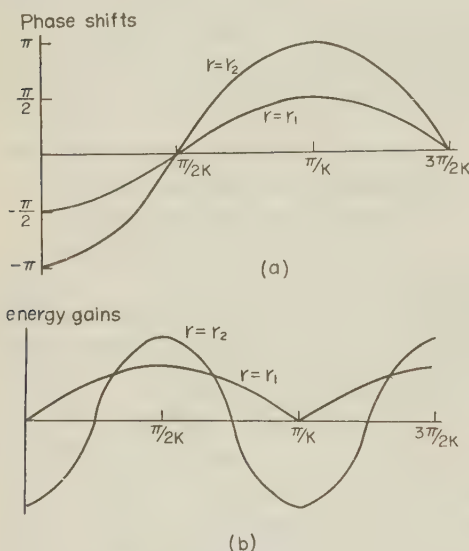


Fig. 3. (a) Phase shifts and (b) energy gains at different radial distances. An ion passing through at r_2 gains no energy on the average.

The gyration phase of the ion passing through r_1 advances against the phase of the R. F. field by π between $z=0$ and $z=\pi/\kappa$, and retards by π between $z=\pi/\kappa$ and $z=2\pi/\kappa$. Therefore, the ion on the average gains energy from the R. F. field**.

* Ions move in z -direction with the constant velocity w_z .

** There may be a case in which ions lose their energy depending on the phase relations between their gyration and the R.F. field. This is the same as in the case of uniform static field.

On the other hand, the ion passing through r_2 gains energy during its movement from $z=0$ to $z=\pi/2\kappa$ and loses same amount of energy during its movement from $z=\pi/2\kappa$ to $z=\pi/\kappa$. On the average, therefore, this ion does not receive energy from the R. F. field.*** (See Fig. 3 (b))

The above statement is valid for the case in which the number of gyration of the ion in one wavelength of the periodic static field is larger than 1, i.e.

$$f_c[(2\pi/\kappa)/w_z] \gg 1.$$

As an example, parameters of the device described in § 4 are as follows:

$$H_0 = 10^4 \text{ gauss}, \quad f_c = 7.6 \text{ MC}, \quad \lambda' = 2\pi/\kappa = 35 \text{ cm}$$

$$H_2 = 950 \text{ gauss}, \quad w_z = 2 \times 10^7 \text{ cm/sec}.$$

Ions are injected at $r_1 = 5.6 \text{ cm}$, and their energy will no longer increase at $r_2 = 12 \text{ cm}$. In this condition, the gyration radius ρ_c of ion is $\rho_c = (r_2^2 - r_1^2)^{1/2} = 10.6 \text{ cm}$. The ion energy E_f corresponding to this gyration radius is 270 keV . About 25 cm will be sufficient for a radius of the vacuum chamber.

Appendix IV. Energy Spectrum of Ions

When an ion passes through the heating section, its velocity, shown in the equation (10), is

$$v_2^2 = v_{\perp}^2 + 2v_{\perp}v_1 \cos \beta + v_1^2, \quad (\text{A. IV. 1})$$

where v_1 and v_2 are respectively the velocities perpendicular to $\mathbf{B}_0$ before and after the ion passes through the heating section and $v_{\perp}$ is the velocity of the ion, gained during its transit through the heating section. The phase difference β takes arbitrary values from zero to π at the equal probability. The transport kernel $f(v_2, v_1)$, which gives the probability that an ion with velocity v_1 becomes velocity v_2 after passing through the heating section, is

$$\begin{aligned} f(v_2, v_1) dv_2 &= \frac{1}{\pi} d\beta = \frac{1}{\pi} \frac{v_2 dv_2}{v_{\perp} v_1 \sin \beta} \\ &= 2v_2 dv_2 / \pi \sqrt{(2v_{\perp} v_1)^2 - (v_2^2 - v_1^2 - v_{\perp}^2)}, \\ v_1 + v_{\perp} &> v_2 > v_1 - v_{\perp}. \end{aligned} \quad (\text{A. IV. 2})$$

Let the number of ions, whose velocity is between v_2 and $v_2 + dv_2$, be $\rho(v_2) dv_2$, then the integral equation determining $\rho(v_2)$ is

*** In this case, ions do not gain energy irrespective of the phase relations between the ion gyration and the R.F. field.

$$\rho(v_2) = \int f(v_2, v_1) \rho(v_1) dv_1 + \delta(v_2 - v_0), \quad (\text{A. IV. 3})$$

where v_0 is the velocity component perpendicular to $\mathbf{B}_0$, of injected ions from the ion source.

The boundary condition is determined in the following way. When the mirror ratio is 2, ions escape from the mirror ends in case $v_2 < w_z$. When the ion energy reaches $E_{\max} = (1/2)mv_{\max}^2$ determined by the dimensions of the container and the strength of D. C. magnetic field, ions are lost after touching the walls of the container. Hence

$$f(v_2, v_1) = 0 \text{ for } v_2 < w_z \text{ and } v_2 > v_{\max}. \quad (\text{A. IV. 4})$$

As an example, computations were carried out on the parameters:

$$w_z = 0.39 v_{\perp}, \quad v_0 = 0.48 v_{\perp}, \quad v_{\max} = 4.94 v_{\perp}.$$

These parameters correspond to the apparatus described in § 3 and the ion injection method of Case II described in Appendix I.* The numerical solution of these equations is shown in Fig. 2.

The same problem may be treated through the Monte Carlo method as follows: with v_0 as a starting point, we make a random walk in a velocity space with a step $v_{\perp}$ using a table of random samples. Then we have the velocity spectrum from the traces of the random walk.

When the point falls into the inside of a circle having a radius w_z , we interpret the ion has escaped from the mirror ends. On the other hand, when the point gets outside of a circle with a radius $v_{\max}$, the ion is regarded as having touched the walls of the container. The calculation was made on the following parameters:

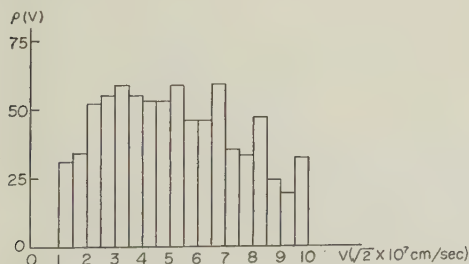


Fig. 4. Velocity spectrum of ions in case of excess acceleration.

* If $w_z \sim v_{\perp}$, $v_0 \sim v_{\perp}$ are chosen, there can be obtained a solution responding to the injection method of Case I.

$$v_{\perp} = 2w_z, \quad v_0 = 1.1w_z, \quad v_{\max} = 10w_z.$$

The result is shown in Fig. 4.

When the energy of ions does not exceed $E_f = (m/2)v_f^2$ (similar to Appendix III), the computation will be made in the same manner as the above. In this case, when the point gets outside of a circle with a radius v_f , the point is replaced on the circle and the random walk is continued. The result, using the same parameters as (A. IV. 6), is shown in Fig. 5.

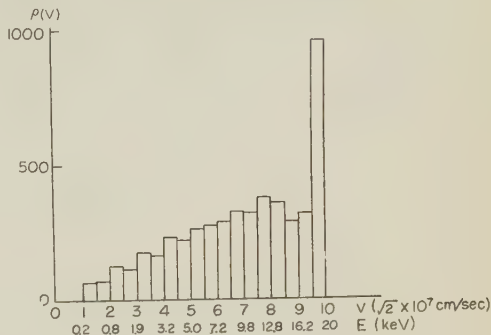


Fig. 5. Velocity spectrum of ions in case of no excess acceleration.

From this we may speculate energy spectrum of ions in the device as described in § 4.

In the case of Appendix III, as the velocity approaches v_f , the step $v_{\perp}$ should approach zero continuously. The computation in this case is complicated and is under way using an electronic digital computer. The energy spectrum is more concentrated around v_f than Fig. 5, because $v_{\perp}$ is small near v_f . The result of this calculation will be published elsewhere.

References

- 1) C. F. Barnett, P. R. Bell, J. S. Luce, E. D. Shipley and A. Simon: Proc. 2nd International Conf. on Peaceful Uses of Atomic Energy, (1958) P/344.
- 2) A. Simon: Phys. Fluids **1** (1958) 495.
- 3) L. Spitzer: *Physics of Fully Ionized Gases* Geneva (Interscience Publ., 1956).
- 4) S. K. Allison: Rev. Mod. Phys. **30** (1958) 1137.
- 5) L. Spitzer: loc. cit. p. 72.
- 6) A. von Engel: *Ionized Gases* (Oxford, 1955) p. 57.
- 7) L. Spitzer: loc. cit. p. 80.
- 8) C. F. Barnett and H. K. Reynolds: Phys. Rev. **109** (1958) 355.
- 9) W. L. Fite and R. T. Brackman: Phys. Rev. **112** (1958) 1141.

- 10) T. H. Stix: *Phys. Fluids* **1** (1958) 308.
 11) A. S. Bishop: *Project Sherwood* (Addison-Wesley Publ., 1958) 56.

- 12) E. T. Whittaker and G. N. Watson: *Modern Analysis* (Cambridge Univ. Press, 1927) 414.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 5, MAY, 1960

The Study of the Optical Properties of Conducting Tin Oxide Films and their Interpretation in Terms of a Tentative Band Scheme*

By Toshihiro ARAI**

*Institute of Physics, College of General Education,
 University of Tokyo, Komaba, Tokyo*

(Received January 6, 1960)

The present report is concerned with an experimental investigation of the influence of free carriers on the optical absorption of SnO_2 , which is an almost perfect insulator in its stoichiometric composition but can be endowed with a semi-metallic conductivity when synthesized by the spraying method. In order to investigate the problem quantitatively, the intrinsic absorption edges of non-conducting films of SnO_2 , SnO , PbO_2 and TiO_2 , as well as that of the conducting tin oxide film (Nesa), were measured at room and liquid nitrogen temperatures. The systematic shift of the edge with the variation of the lattice constants of these oxides was confirmed experimentally with the exception of Nesa, in which case the edge was always found ca. 0.1 eV higher in energy than that of the non-conducting SnO_2 film. This latter phenomenon was interpreted as the filling-up effect of the bottom of the conduction band by the free carriers, in accordance with the theory of Fan et al presented for the case of InSb . With the aid of the other auxiliary electrical and thermal experiments performed, a tentative energy band scheme of the conducting tin oxide was proposed.

§ 1. Introduction

The transparent conductor is an interesting material because of its versatile utilities as well as its physical properties. In the previous paper, we have reported some results on the optical and electrical properties of "Nesa", which is the best known example of the transparent conductor.¹⁾²⁾ According to our results, it is essentially the polycrystalline SnO_2 , and from the electrical properties it is concluded to be a semiconductor of n -type with the free carrier density of

$7 \times 10^{18} \sim 1.7 \times 10^{19} \text{ cm}^{-3}$. The impurity scattering is mainly responsible for the electrical resistance and the free carrier density is independent of the temperature, indicating that the degeneracy is present. The transparency in the visible region of the spectrum is explained by the fact that the threshold of the absorption by the free carriers is lying in the infrared region because of their density just described. These data were treated by the Drude-Kronig formula and the effective mass m_c^* of the electron was found to be about 0.15m. In the present paper, we shall try to elucidate the natures of "Nesa" comparing with the experimental results on the various oxides of IV group obtained by the same method of preparation

* This paper was submitted to the University of Tokyo in partial fulfilment of the requirements for the degree of Doctor of Science.

** Present address: Electrical Communication Laboratory, Kichijoji, Tokyo.

as “Nesa”, and “Nesa doped with Sb”, and the study of transient behaviors from SnO to SnO₀.

§ 2. Experimental Results: Optical Properties.

1). *Visible and ultra-violet region.*
Transmission and reflection measurements over the wavelength region from 0.22 to 0.7μ were carried out by a small quartz spectrometer. Transmissivity and reflectivity of non-conducting SnO₂, “Nesa”,* TiO₂, PbO₂, and SnO are plotted against the wavelengths in Fig. 1. SnO film was obtained by the vacuum evaporation of the chemically prepared SnO powder. The Sample denoted as non-conductive SnO*₂, distinguished from Nesa, was obtained from SnO film or Nesa by heating in the air until

it became nonconductive. Refractive indices of those materials determined from the spectral reflectivity and transmissivity in the transparent region³⁾ are shown in Fig. 2, with the values obtained by Abelé’s method⁴⁾ where the dotted line is drawn with the aid of values found in I.C.T. The thickness of the of the film was estimated by Tolansky’s multiple beam interferometric method.⁵⁾ It is clearly seen that refractive index of our sample is considerably smaller than those found in the table, probably due to the samler density of our sample resulting from our method of preparation. If we assume that the Lorentz-Lorenz equation is valid for our

Table I. $\frac{N-N_s}{N} \times 100$ of several materials

	$\frac{N-N_s}{N} \times 100$
NeSa	4 ~ 6
SnO ₂	4 ~ 6
TiO ₂	12 ~ 17
PbO ₂	

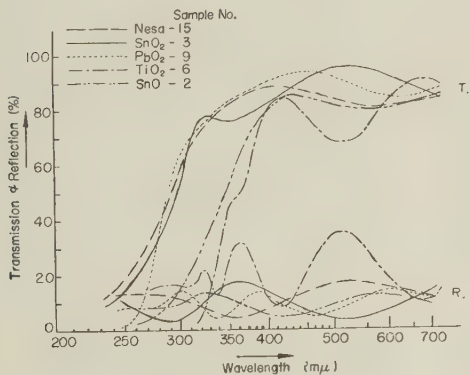


Fig. 1. The spectral transmissions and reflections of several oxides of IV group.

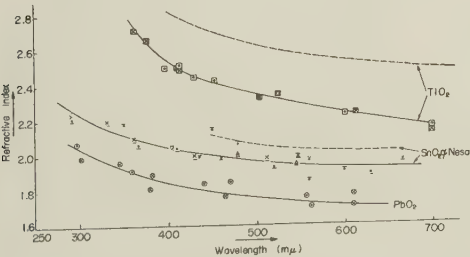


Fig. 2. The refractive index plotted against the wavelength. The measured values are shown by ● (Spectroscopic), × (Tolansky’s method) and △ (Abelé’s method), where the points shown by under bar represent Nesa; the upper bar, SnO₂, the rectangle, TiO₂; the circle, PbO₂. The dotted lines are drawn with the aid of values found in I.C.T..

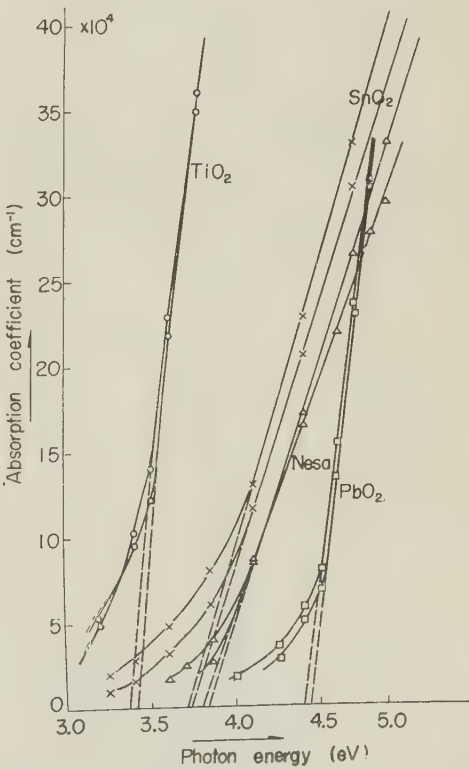


Fig. 3. Absorptions of Nesa, PbO₂, TiO₂ and SnO₂ at room temperature.

* Here after, we will distinguish non-conductive SnO₂ and conductive SnO₂ by denoting the former simply as SnO₂ and the latter as Nesa.

sample, the density N is proportional to $(n^2-1)/(n^2+2)$. So, if we define the density reduction of the crystal by D ,

$$D = \frac{N - N_s}{N} = \left(\frac{n^2 - 1}{n^2 + 2} - \frac{n_s^2 - 1}{n_s^2 + 2} \right) / \frac{n^2 - 1}{n^2 + 2}$$

where letters with suffix s refer to the sample and ones without suffix refer to the normal crystal, the values of D obtained by this formula are give in Table I.

Optical properties of Nesa and SnO_2 in uhe visible region of the spectrum agree quite well as overserved in Fig. 1 and Fig. 2, indicating that the basic material of Nesa is SnO^2 as reported previously. In the ultra-violet

Table II. Absorption edge.

	Absorption Edge (eV)
NeSa	3.82 ± 0.030
SnO_2	3.71 ± 0.025
TiO_2	3.46 ± 0.022
PbO_2	4.45 ± 0.032

region in which the intrinsic absorption occurs, however, there are some differences between the absorption behaviors of Nesa and SnO_2 . In hopes of elucidating the origin of these differences, we studied the natures of the corresponding fundamental absorption of some reference materials such as SnO ,

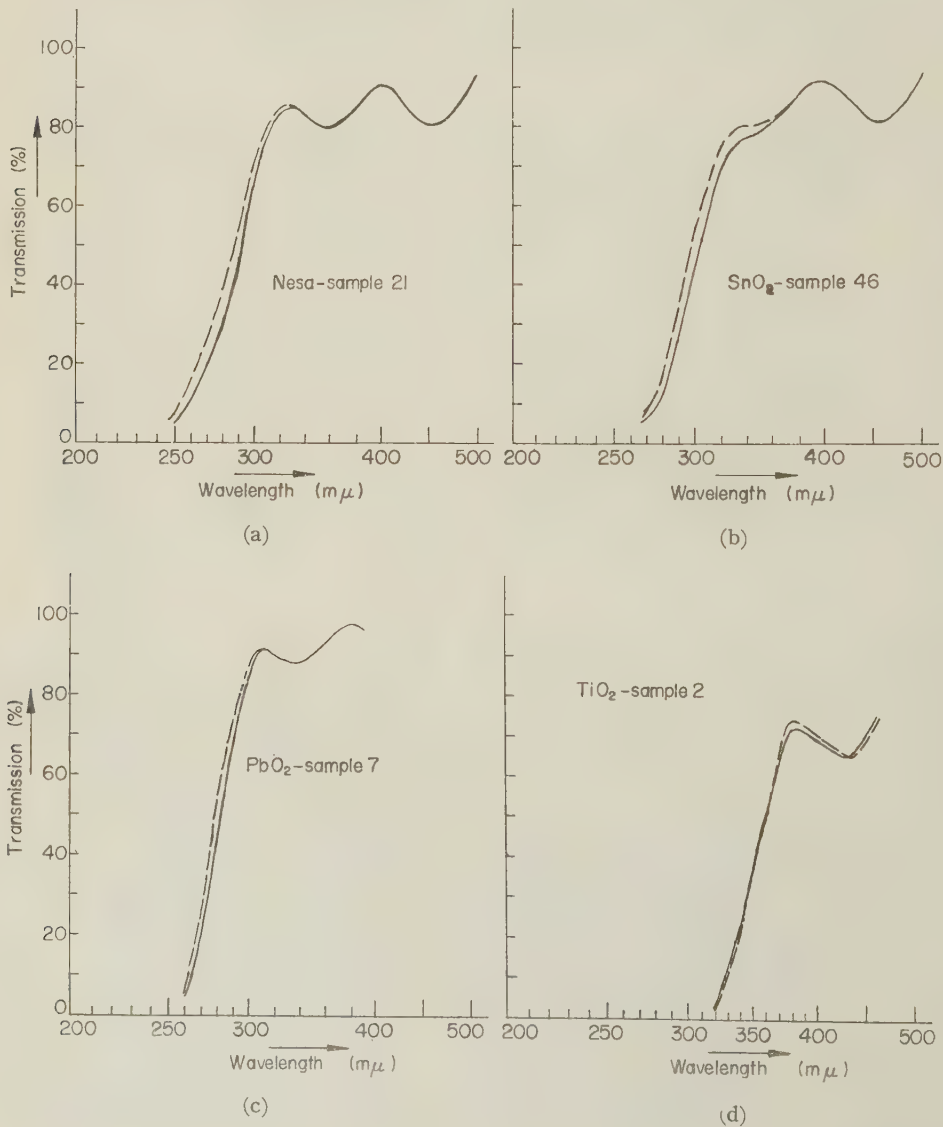


Fig. 4. Temperature change of transmission. Full line; at +30°C, Dotted line; at -145°C.

PbO₂, and TiO₂. These results are summed up in Fig. 3 and Table II.

The absorption edge of Nesa would be expected to have the intermediate position between SnO₂ and SnO, or at least there would be no reason to occur at higher energy than SnO₂ if we assume that Nesa is a semiconductor of the Sn excess type made of SnO₂. Nevertheless, it does occur always at higher energy by about 0.1 eV in our experimental results, so we have to look for another interpretation. We can explain this phenomenon by the assumption that the bottom of the conduction band is occupied to rather high energy states and the allowed transition from the valence band begins at correspondingly higher energy than the forbidden energy gap. This interpretation is similar to the case of InSb which was investigated by Fan et al,⁶⁾ and will be discussed in detail in the later part of this paper.

Since the temperature dependence of the absorption edge seems, to be of interest in regard to these aspects, the absorption curves of SnO₂, PbO₂, TiO₂, and Nesa at lower temperatures are shown in Fig. 4. Coefficients for the shift of the absorption edge with the temperature, taken from these curves are given in the Table III.

Table III. Temperature change of absorption edge.

	$\Delta E_g/\Delta T$ (eV/°K)
NeSa	$-2.0 \times 10^{-4} \pm 5 \times 10^{-5}$
SnO ₂	$-2.0 \times 10^{-4} \pm 4 \times 10^{-5}$
PbO ₂	-1.7×10^{-4}
TiO ₂	-5.8×10^{-5}

Though there are several different definitions of the absorption edge widely used by a number of authors,^{7),8),9),10),11)} it seems that none of them are definitely accepted. Therefore on determining the absorption edge, as it is seen in Fig. 3 we have adopted the method of extrapolating the absorption curves drawn in the linear scale. We determined it by extending the linear portion of the absorption curve which corresponds to the value of α between $5 \times 10^4 \sim 2 \times 10^5 \text{ cm}^{-1}$ and taking its intersection with the line $\alpha=0$. The reasons for our preference were the practical convenience due to the linearity of

the absorption curves in this direct transition region and the consideration that the influence of the indirect transition is rather to be eliminated for our present purpose and saturation does not occur in this region.^{10),12),14),14)}. In Fig. 5, the position of the absorption edges for these materials (Table II) are plotted against the lattice parameter $\sqrt[3]{a^2c}$ for the convenience to the analysis which will be given later.

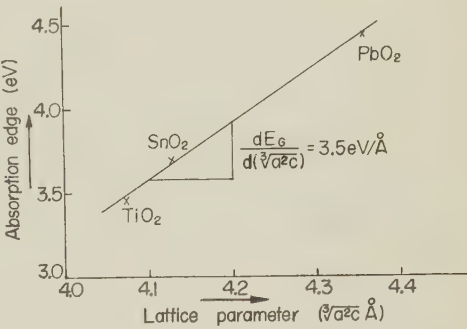


Fig. 5. The Shift of absorption edge as a function of lattice constant.

2) Infrared region

We have reported in the previous article that differences observed in the infrared transmissivity and reflectivity of Nesa and SnO₂ are attributed to the difference of the density of free electrons. Here, we have carried out another experiment on Nesa doped with 1% Sb in order to confirm our interpretation. Fig. 6 shows the transmissivity and the reflectivity of SnO₂, SnO, and Nesa (1% Sb)

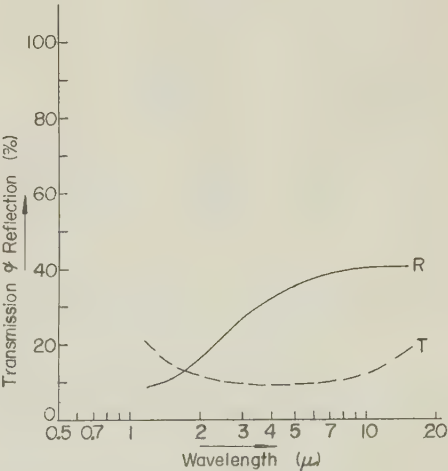


Fig. 6a. Transmission and reflection curves of Nesa doped with Sb (1%).

Table IV. Electrical data of impurity doped Nesa at room temperature.

	σ ($\Omega^{-1}\text{cm}^{-1}$)	$\frac{R}{\text{cm}^3}$ ($\frac{\text{coulomb}}{\text{coulomb}}$)	Thickness $d(\mu)$	m^*	τ (sec)	ν_p (sec $^{-1}$)	ν_A (sec $^{-1}$)
SnSb-13	347	-0.011	0.203	m	2.14×10^{-15}	2.13×10^{14}	7.45×10^{13}
				0.30 <i>m</i>	6.42×10^{-16}	3.89×10^{14}	2.48×10^{14}
				0.10 <i>m</i>	2.14×10^{-16}	6.73×10^{14}	7.45×10^{14}
SnSb-7	944	-0.0055	0.0505	m	2.97×10^{-15}	3.02×10^{14}	5.36×10^{13}
				0.30 <i>m</i>	8.91×10^{-16}	1.74×10^{14}	1.79×10^{14}
				0.10 <i>m</i>	2.97×10^{-16}	9.54×10^{14}	5.36×10^{14}

Table V. Calculated values of refractive index and extinction coefficient as functions of effective mass of conduction electron and light wavelength. (SnSb-13)

$\lambda(\mu)$	$m^*=m$		$m^*=0.3m$		$m^*=0.1m$	
	n	k	n	k	n	k
0.6			1.77	0.0677	1.761	0.2377
0.8					1.712	0.3775
1.0	1.699	0.0353	1.56	0.266	1.708	0.5128
1.25					1.735	0.6618
1.5	1.517	0.1232			1.775	0.7981
2.0	1.318	0.3043	1.53	0.931	1.883	1.034
3.0	1.123	0.9661	1.80	1.45	2.108	1.417
4.0	1.284	1.569			2.326	1.726
6.0	1.778	2.358			2.717	2.229
10.0	2.651	3.289			3.376	2.998
15.0	3.487	4.067			4.056	3.746

in the infrared region. Refractive index of Nesa in the near infrared region in which we are now concerned is considered to be controlled by the fundamental absorption and the absorption by the free electron. We calculated the refractive index n and the extinction coefficient k from the optical data just described and the electrical measurements shown in Table IV, utilizing the Drude-Kronig relation,¹⁵⁾ where the effective mass m_e^* of the electron were taken as the parameter. The results are shown in Table V. In Fig. 7, the transmissivity and the reflectivity of Nesa (1%*Sb*) obtained from the values of n and k with the formulas for thin absorbing films¹⁶⁾ are plotted. We estimated from these results the value of the electronic effective mass of Nesa (1% *Sb*), to be 0.15 *m*, nearly equal to Nesa without *Sb* impurity.

In Fig. 6, we also illustrated the absorption of powdered SnO_2 and SnO samples in

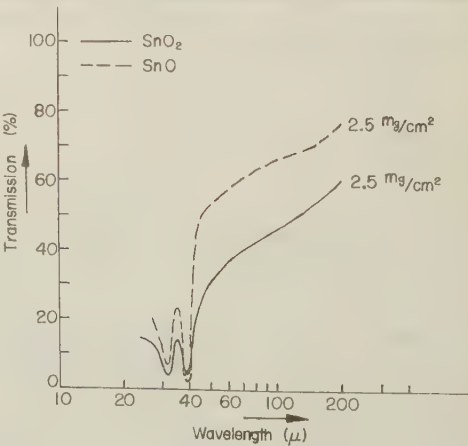


Fig. 6b. Transmission of SnO_2 and SnO in the infrared region.

the far infrared region which is measured by the courtesy of Prof. Yoshinaga of Osaka University. The two absorption curves show rather remarkable resemblance and absorp-

tion peaks presumably corresponding to lattice vibrations of SnO bonds are observed from 30 to 40 μ in both materials. A closer examination reveals that SnO shows the more intense absorption and might be more ionic than SnO₂. We shall not, however, discuss the point in greater detail, because our measurements were carried out in the room temperature and with powdered samples.

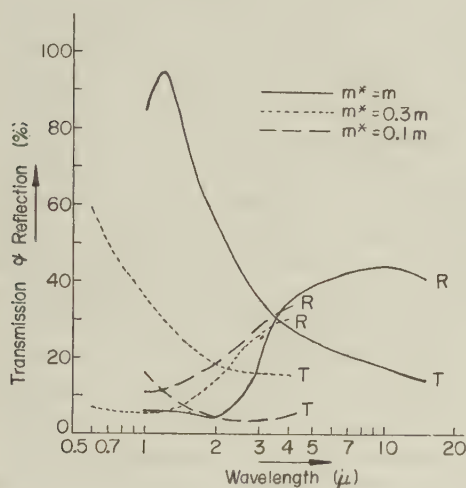
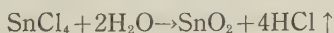


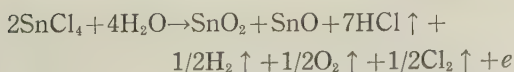
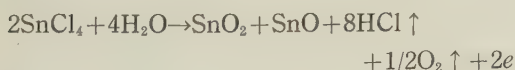
Fig. 7. The calculated transmission and reflection curves of Nesa doped with Sb (1%). (cf. Fig. 6a).

§ 3. Electrical Properties.

The reaction by which Nesa is formed would be writted as;



If this reaction is completely over, Nesa would be an insulator as well as SnO₂. Two origins would be conceivable for the conductive behavior of Nesa. One of them is the deficiency of oxygen and another is the residual chlorine ion as the impurity left after the incomplete reaction. Each of these reaction is represented by



In order to determine which is the dominant process for supplying free electrons, we have carried out the following experiments.

First, the change of the electrical resistivity was measured over a cycle of thermal treatment in the air, and the curve for Nesa

is shown in Fig. 8. It is suggested at a glance of Fig. 8 that the reversible change

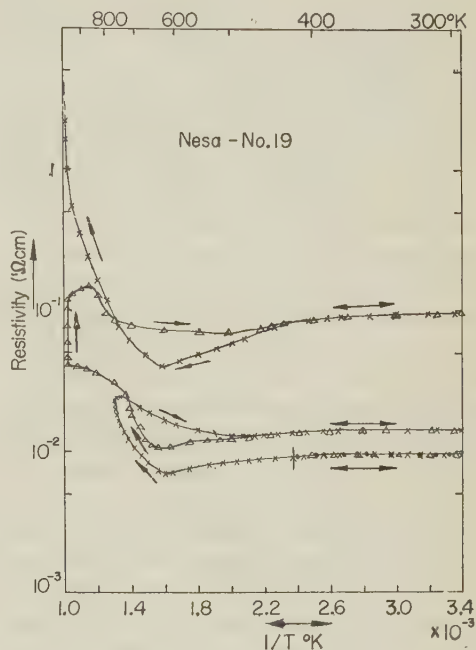


Fig. 8. Resistivity of Nesa as a function of $1/T$.

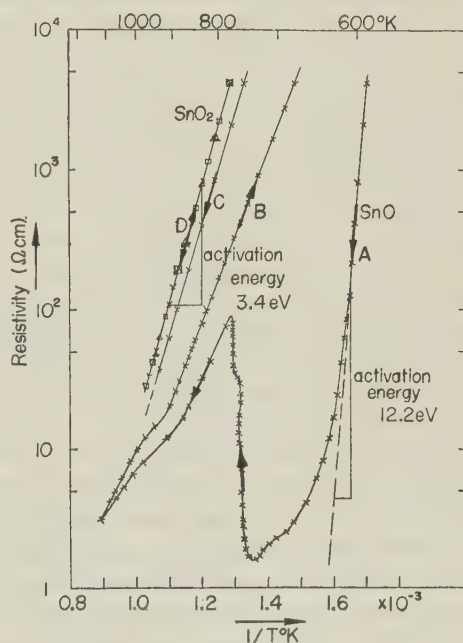


Fig. 9. Resistivity change during heat treatment of SnO. The irreversible change would correspond to the transition process from SnO to SnO₂. The abscissa is given in reciprocal temperature. The rate of temperature rise was ca. $100^\circ\text{C}/\text{hour}$.

under 250°C and the irreversible change above 250°C take place. Fig. 9 illustrates the change of the resistivity during the heat treatment in the air to transform the vacuum evaporated SnO film into SnO₂. The rate of temperature rise was *ca.* 100°C/hour.

The decrease of resistivity with rising temperature observed in Part A of the curve may be interpreted as the two superposing processes, one of which is the formation of donors by the initial oxidation of SnO, and the other is the increasing thermal excitation of electrons from the valence band. As the oxidation proceeds further, it appears that donors are no more formed but rather decrease gradually (Part B and C), and non-conductive SnO₂ is formed at the final stage of oxidation (Part D), where only the thermal excitation of electrons across the energy gap is to be observed. The activation energy for these processes are estimated as 3.4 ± 0.06 eV for SnO₂ (part D) and 12 eV for SnO (part A). Compared with this result for SnO₂, the value determined optically is slightly (*ca.* 0.3 eV) larger. This would indicate that the conduction band minima and the valence band maxima do not occur at the same value of *K*. On the other hand, in Part A, the process is irreversible and the excitation energy optically determined is considerably smaller than the value from the thermal analysis. The latter depends greatly on the rate of temperature rise, because of the resistivity decrease of various degree in the process of oxidation. Therefore the apparent activation energy obtained by the thermal analysis in this region cannot have the definite physical meaning. It is apparent from the experiment that the part of its free electron is related to the oxygen deficiency, but we could get by no means the specimen showing as good conductivity as Nesa by the heat treatment. The best conductivity we have observed through this treatment is the order of 10^{-3} ohm⁻¹ cm⁻¹ at the room temperature. Furthermore, oxidation of SnO required rather little time, i.e. 4 to 5 hours, at comparatively lower temperatures (*ca.* 500°C), for completing its reaction to form SnO₂ from SnO, whereas it took much longer time to make the insulating SnO₂ by oxidation of Nesa even at higher temperatures. Therefore, it seems to us that Nesa is not a simple oxide

semiconductor of the reduction type.

Next, we have made an experiment in order to check another possibility, that is, the effect of the residual Cl impurity. We heated samples of SnO₂ and SnO in the chlorine vapor. The electrical resistivity of SnO films treated in Cl₂ reduces to several hundred ohm cm in a few hours, but the films are easily wiped away. In the case of SnO₂, the resistivity reduces to about several thousands ohm cm in two hours and the films can not be wiped, but they can also be wiped off after five or six hours when their resistivity decreases to several hundreds ohm cm. Up to the present, the thin film which exhibits as good conductivity as Nesa could be made by no ways but the spraying method. It is widely known, however, that the films of TiO₂¹⁷⁾, In₂O₃¹⁸⁾ and CdO¹⁹⁾ prepared by sputtering and succeeding heat treatments, show considerably good conductivity. Thus, from our preliminary attempts, no decision could be made about what is the origin of free electron in Nesa.

It is to be noted that the films of PbO₂ and TiO₂ prepared by the equivalent method to Nesa, sintered SnO₂ and vacuum evaporated SnO are all insulators having the resistivities of larger than 10⁵ ohm cm, which was our limit of measurements.

If Sb is put into Nesa as the impurity, maximum conductivity is attained when its concentration in the weight is 1%, and the conductivity decreases remarkably as the concentration becomes larger. This phenomenon, which was already reported by Akiyoshi et al.^{20), 21)} is probably caused by the increase of impurity scattering, which would also be responsible for the behavior of In-doped Nesa.²²⁾ On heating above 800°C, Nesa doped with Sb is very stable and neither its conductivity nor optical properties are subject to any remarkable change in contrast with Nesa without doping. Usually Nesa opaque and blackish when the concentration of Sb increases.

§ 4. Determination of the Hole Effective Mass.

The most prominent effect of temperatures to the absorption edge would be observed for the absorption to the indirect transition. Our measurements, however, are confined to the region where only the absorption by the

direct transitions are important because of their order of magnitude. Therefore, the shift of the absorption edge observed in our measurements should be considered as the variation of the forbidden energy gap ΔE_g by the temperature variation. Temperature variations cause the shift of energy bands through

- 1). volume dilatation
- 2). intensity of the lattice vibration.

The first effect was treated by Shockley and Bardeen²³⁾ for the the elemental semiconductors and the second was discussed in detail by Fan and by Muto and Oyama.²⁴⁾ In practice, both the polar and nonpolar crystals are treated in a similar way, that is, taking account of the carrier mobility determined by the lattice scattering in the former case and calculating the change of the electron-lattice interaction energy of the crystal resulting from excitation of electrons in the latter case. The effective energy gap E_g for sufficiently high temperatures is given by¹¹⁾

$$E_g = E_0 + \left(\frac{\partial E_g}{\partial P} \right)_T P + \left\{ \left(\frac{\partial E_g}{\partial T} \right)_V - \left(\frac{\beta}{\alpha} \right) \left(\frac{\partial E_g}{\partial P} \right)_T \right\} T$$

where P , T and V refer to pressure, absolute temperature, and volume, respectively, while α is the compressibility and β represents the thermal coefficient of volume expansion. The first term of the right hand is $E_0 = E_{g0} + E_{ig}$, i.e., the sum of E_{g0} , the energy gap at 0°K, where atoms are quiescent at their equilibrium position, and E_{ig} , the correction for the energy gap taking into account the variation of the electron-lattice interaction energy according to excitation of electrons at 0°K. Therefore, the quantity to be compared with our measurements is

$$\left(\frac{\partial E_g}{\partial T} \right)_P = \left(\frac{\partial E_g}{\partial T} \right)_V - \left(\frac{\beta}{\alpha} \right) \left(\frac{\partial E_g}{\partial P} \right)_T \quad (1)$$

where the first term of the right hand is the coefficient of electron-lattice interaction and the second term is the coefficient of the change due to the volume dilatation. Radkowsky²⁵⁾ and Fan²⁶⁾ derived a formulation of $(\partial E_g / \partial T)_V$ for the diatomic polar crystal as follows:

$$\Delta E_g = - \frac{2\pi(e^*e)^2}{\Omega M} \cdot \left(\frac{2}{\hbar \omega_l^3} \right)^{1/2}.$$

$$\frac{(m_c^{*1/2} + m_v^{*1/2})}{\exp[\hbar \omega_l / kT]^{-1}} \quad (2)$$

where Ω is the volume of the unit cell, M is the reduced atomic mass, while m_c^* , m_v^* are the effective masses of the electron and the hole, respectively. ω_l is the longitudinal fundamental frequency of the lattice vibration belonging to the optical mode and related to the Reststrahl frequency ω_l by²⁷⁾

$$\omega_l = \left(\frac{\omega_0}{\epsilon_\infty} \right)^{1/2} \omega_t.$$

e^* is the effective ionic charge given by

$$4\pi e^{*2} = M \Omega \omega_l^2 \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)$$

in which ϵ_0 , ϵ_∞ are the dielectric constants for zero and optical frequencies, respectively. Now, we shall use these relation to determine the effective mass of the hole in SnO_2 . First, it is required the value of $(\beta/\alpha)(\partial E_g / \partial P)_T$ which could not be measured directly in our laboratory. We estimated it from the value of $\partial E_g / \partial l$ determined from the plot of the absorption edge shift against the lattice constants of several materials of the same crystal form and value of $[\sqrt[3]{a^2c} - \sqrt[3]{(a+\Delta a)^2(c+\Delta c)}]$ (Fig. 5), the decrement of the lattice constants with decreasing temperatures. Thus we get

$$\begin{aligned} \beta/\alpha \cdot (\partial E_g / \partial P)_T &= \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial L}{\partial P} \right)_T \left(\frac{\partial E_g}{\partial l} \right)_l \\ &= \frac{\beta}{\alpha} \cdot \frac{\alpha}{3} \cdot l \cdot \frac{\partial E_g}{\partial l} \\ &= 4.9 \times 10^{-5} \text{ eV}^\circ\text{K}. \end{aligned}$$

Using Eq. (1) and Table III, we get

$$\begin{aligned} (\partial E_g / \partial T)_V &= (\Delta E_g / \partial T)_P + (\beta/\alpha)(\partial E_g / \partial P)_T \\ &= -2.0 \times 10^{-4} + 4.9 \times 10^{-5} \\ &= -1.51 \times 10^{-4} \text{ eV}^\circ\text{K} \quad (3) \end{aligned}$$

When the calculation is made by Eq. (2), it should be noted that two values of ω_l exist as clearly seen in Fig. 6, corresponding to the two types of Sn-O bond in the SnO_2 crystal. We treated these two modes of the lattice vibration independently and neglected their coupling which might be expected when they interact with the electron. Then the total effect is given by the sum of their independent contribution to the energy. Table VI shows the results, which are the

Table VI. The table to calculate $(\partial E_g/\partial T)_v$.

ω_l	$5.66 \times 10^{13} \text{ cm}^{-1}$	$4.83 \times 10^{13} \text{ cm}^{-1}$	§ 2-1
ϵ_0	23.6	23.6	J.A. p. 40
ϵ_∞	3.92	3.92	§ 2-2
ω_e	$1.39 \times 10^{14} \text{ cm}^{-1}$	$1.18 \times 10^{14} \text{ cm}^{-1}$	$\sqrt{\epsilon_0/\epsilon_\infty} \cdot \omega_l$
$4\pi e^{*2}/M\Omega$	$4.10 \times 10^{27} \text{ cm}^{-2}$	$2.92 \times 10^{27} \text{ cm}^{-2}$	$\omega_l^2(1/\epsilon_\infty - 1/\epsilon_0)$
$\sqrt{2/\hbar\omega_l^3}$	2.66×10^{-8}	3.41×10^{-8}	$\text{erg}^{-1/2}\text{sec}^{-1/2}\text{cm}^{3/2}$
$2\pi e^{*2}\sqrt{2m}/\Omega M\sqrt{\hbar\omega_l^3}$	2.37×10^{-1}	2.16×10^{-1}	eV
$\exp(\hbar\omega_l/kT)$	34.295	20.03	at $T=300^\circ\text{K}$
$\exp(\hbar\omega_l/kT)$	1177.4	399.59	at $T=150^\circ\text{K}$
$1/\exp(\hbar\omega_l/kT) - 1$	0.03003	0.05255	at $T=300^\circ\text{K}$
$1/\exp(\hbar\omega_l/kT) - 1$	0.00085	0.00251	at $T=150^\circ\text{K}$
$-dE_g/dT$	$4.6 \times 10^{-5} \text{ eV}/^\circ\text{K}$	$7.2 \times 10^{-5} \text{ eV}/^\circ\text{K}$	mean value between $300^\circ \sim 150^\circ\text{K}$

averages of the values for 150°K and 300°K . Now, we get

$$(\partial E_g/\partial T)_{\text{v calcd.}} = -1.18 \times 10^{-4} \times \left[\left(\frac{m_o^*}{m} \right)^{1/2} + \left(\frac{m_v^*}{m} \right)^{1/2} \right] eV/^\circ\text{K} \quad (4)$$

If we substitute the value of Eq. (3) and put $m_o^*=0.15m$ into the relation, we get the value of the effective mass of the hole as;

$$m_v^*=0.82m.$$

§ 5. Discussions about the Energy Band Structures of Nesa and SnO_2 .

Nesa was found to be a semiconductor of n -type substantially made of SnO_2 from our experiments. Free electrons are to be supplied by some imperfections such as the impurity atoms or the lattice defects, which should be observed in the absorption measurements. Although we have briefly pointed out that in § 2, we shall give more detailed discussions here.

The level density is estimated to be of comparable order as the free electron density which is about 10^{19} cm^{-3} , and it would give the absorption constant $\alpha=5 \times 10^4 \text{ cm}^{-1}$, if we assume the broadening of the level $\Delta\hbar\omega=0.02 \text{ eV}$ and the oscillator strength to be unity. Thus, some effects are expected to be observed if the impurities of such large density exist. As well, the results of the electrical measurements are not favorable to the existence of impurity levels, because the carrier density suffers no appreciable change by lowering temperatures.^{1), 22)} It is known that the activation energy reduces with in-

crease of impurity density in Ge and Si, and, for example, in Si, it becomes effectively zero as the impurity levels merge in to bottom of the conduction band.²⁸⁾ It is probably due to the increased interaction between the impurity atoms when they are brought together, or the increased shielding effect of impurity centers by the free electrons.²⁹⁾ If the situation is similar in our case, the impurity levels and the conduction band might interact to each other and merge into one indistinguishable band, and the whole conduction band at the same time will move up or down.³⁰⁾ Though it seems somewhat inconsequent that $(\partial E_g/\partial T)_v$ is the same for Nesa and SnO_2 , it is understood by taking into account the degeneracy which is also supported by the electrical measurements. We have to conclude that the locations of the extrema of the conduction band and the valence band do not coincide in the K -space because the values of activation energy obtained from the measurements of the absorption edges and the thermal analysis of the conductivity are different. We shall here propose a band model which will explain not only this difference but also the shift observed between the absorption edge of Nesa and that of SnO_2 . We assume that the constant effective mass approximation is valid for each of the conduction band and the valence band. The proposed model is illustrated in Fig. 10. The energy in the conduction band measured from the valence band is given by

$$E=E_0+(\hbar^2k_0^2/2m_o^*)+\hbar^2(K-K_0)^2/2m_o^* \quad (5)$$

From the minimum condition of E , i.e.

$\partial E/\partial k_0=0$

$$K=(m_e^*+m_v^*)/m_v^* \tag{6}$$

Substituting Eq. (6) into Eq. (5), we get

$$E_{\min.}=E_0+\frac{\hbar^2 K_0^2}{2m_v^*}\left(1+\frac{m_e^*}{m_v^*}\right). \tag{7}$$

Solving this equation for k_0 ,

$$k_0=\sqrt{\frac{2(E_{\min.}-E_0)}{\hbar^2}\cdot\frac{m_v^*}{(1+m_e^*/m_v^*)}}.$$

Using the values described before, $m_v^*=0.82m$, $m_e^*=0.15m$, $E_{\min.}=3.71$ eV, $F_0=3.4$ eV, K_0 and K are determind as

$$K_0=2.68\times10^7\text{ cm}^{-1}$$

$$K=3.07\times10^7\text{ cm}^{-1}$$

where we assumed that the shaps of conduction bands for Nesa and SnO₂ are the same and paralle to each other.

Now that we have determined the relative position of the conduction band and the

valence band of SnO₂ and the location of the minimum energy separation where the optical excitation commences, we want to explain the difference observed between the absorption edges of Nesa and SnO₂. The Fermi level ζ of Nesa lies at 0.09~0.17 eV above the bottom of the conduction band, for the carrier densities obtained from the electrical measurements are $7\times10^{18}\sim1.7\times10^{19}\text{ cm}^{-3}$. Hence, the electrons fill the conduction band up to the energy to which the corresponding wave numbers range from 8.0×10^6 to $4.6\times10^6\text{ cm}^{-1}$. Since electrons can not be excited to this filled region, the threshold of optical excitation must move to the point **B'E'**, while the energy in the valence band increases by $\Delta E_x=0.09\sim0.01$ eV correspondng to $K_x=2.61\times10^7\sim2.27\times10^7\text{ cm}^{-1}$. Then the absorption edge of Nesa should be 0.043 eV higher than non-conducting SnO₂, where as the optical measurements give the value 0.11 eV. If this discrepancy is attributed to the shift of the whole conduction band ΔE_x caused by its overlapping with the impurity levels, it

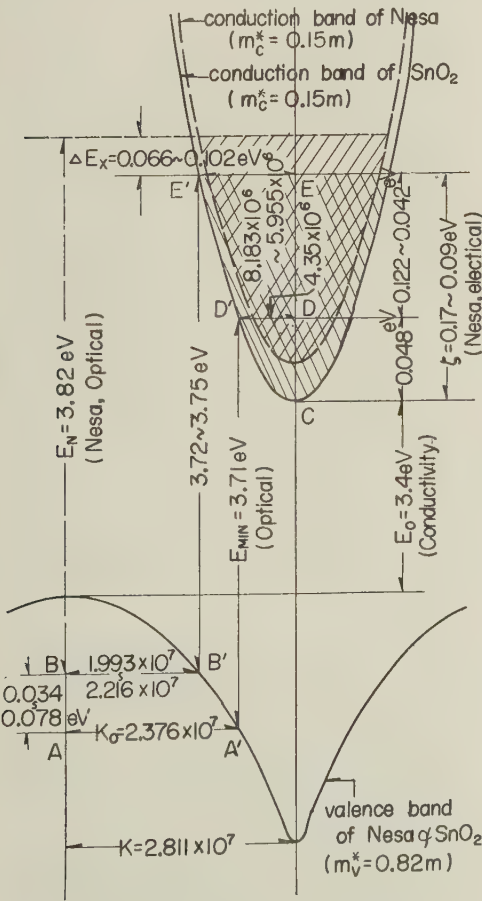


Fig. 10. Energy bands scheme of Nesa and SnO₂. The effective mass of SnO₂ was assumed to be same as Nesa.

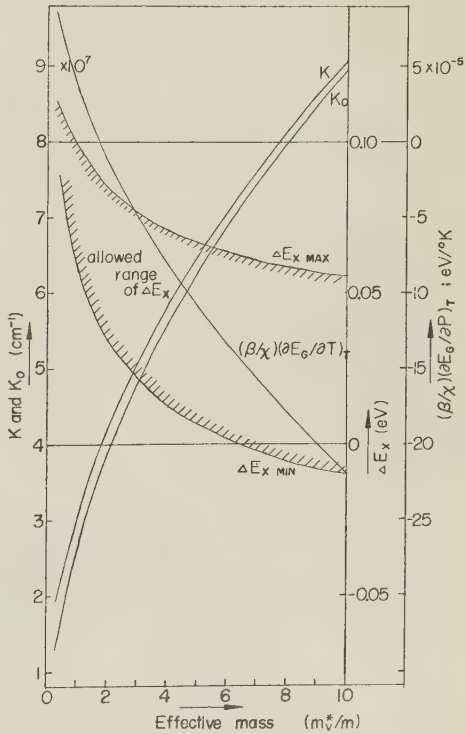


Fig. 11. ΔE_x , K , K_0 and $(\beta/\chi)(\partial E_g/\partial p)_T$ as a function of effective mass of hole. The suffixes of ΔE_x denote the upper and lower limits of experimental error, respectively.

should be 0.067 eV, which is somewhat too large. However, taking account of rather rough approximations employed in deriving m_v^* , it would not be appropriate to discuss the value of ΔE_x in further details. We could, however, say that the value of ΔE_x obtained was not so unreasonable as to prove the method used to derive m_v^* to be inadequate.

In order to check the validity of the value of m_v^* determined in §4, we computed ΔE_x , K , K_0 and $\frac{\beta}{\chi} \left(\frac{\partial E_g}{\partial P} \right)_T$ to the various values of m_v^* . The results are illustrated in Fig. 11, for the values of m_v^* ranging from 0.5m to 10m. The shift of the absorption edge depends remarkably on the density of the free electron for the larger values of m_v^* , while it becomes almost independent of the carrier density and the shift is entirely due to the movement of the band as a whole when m_v^* is less than 0.5m. The upper limit of m_v^* just given corresponds to the shift of 0.07 eV which is slightly larger than the sum of errors in determining the absorption edges for Nesa, 0.03 eV, and SnO₂, 0.025 eV. Thus, our measurements are not so accurate as to estimate the effect of the change of carrier density on the absorption edge. Numerical values given in our model are, therefore, the mean values which obtained from the experiments. The values of $\frac{\beta}{\chi} \left(\frac{\partial E_g}{\partial P} \right)_T$ corresponding to the extrema of m_v^* are $+7 \times 10^{-5}$ and -22×10^{-5} eV/ $^{\circ}$ K. In these and other crystals this quantity is usually about 5×10^{-5} eV/ $^{\circ}$ K, giving the value of m_v^* as $0.075m \sim 3m$. Since ΔE_x is positive up to $m_v^*=10m$, the conduction band will move toward higher energy when the density of the impurity increases.

We assigned the minimum of the conduction band to $K=0$ and the top of the valence band off the origin under the assumption that the conduction band of SnO₂ would be composed of s state and the valence band may be of p or d character.

Acknowledgments.

The authors are very grateful to Prof. Takagi and Dr. Kuriyama for their assistance in the X-ray measurements. We also wish to thank Prof. Kudo of Institute for Optical

Research, Tokyo University of Education and Prof. Yoshinaga of Osaka University for their helps in the infrared experiments. The authors are much indebted to Prof. Yamashita and Dr. Kurosawa of Tokyo University for discussions on the analysis.

Our thanks are due to Prof. Ishiguro, Mr. Sasaki and Mr. M. Imai of our laboratory for their cooperation and advice with respect to these experiments and analysis.

References

- 1) K. Ishiguro, T. Sasaki, T. Arai and I. Imai: J. Phys. Soc. Japan **13** (1958) 296.
- 2) K. Ishiguro, T. Sasaki, T. Arai and I. Imai: J. Phys. Soc. Japan **13** (1958) 755.
- 3) M. Kiuchi: *Optical Research of the Thin Films* (Iwanami Press, 1954) 48 (in Japanese).
- 4) F. Abelés: J. phys. radium **11** (1950) 366.
- 5) S. Tolansky: *Multiple-beam Interferometry of Surfaces and Films* (Oxford at the Clarendon Press, 1948).
- 6) H. Y. Fan and W. G. Spitzer: Phys. Rev. **106** (1957) 882.
- 7) R. Braunstein, A. R. Moore and F. Herman: (1955) Phys. Rev. **109** (1958) 695.
- 8) F. Urbach: Phys. Rev. **92** (1954) 1324.
- 9) W. C. Dash and R. Newmann: Phys. Rev. **99** 1151.
- 10) G. G. Macfarlane and V. Robert: Phys. Rev. **97** 1714, Phys. Rev. **98** (1955) 1865.
- 11) H. Y. Fan: Repts. Progr. Phys. **19** (1956) 107. D. U. Dexter: Photo. Conference (John Wiley and Sons, Inc., New York, 1954), 155. J. Bardeen, F. J. Blatt, and L. H. Hall: Photo. Conference. p. 146. G. Dresselhaus: Phys. Rev. **100** (1955) 580.
- 12) H. Y. Fan, M. L. Shepherd and W. G. Spitzer: Photo. Conference, p. 184.
- 13) J. N. Humphrey and R. L. Petritz: Phys. Rev. **105** (1957) 1192.
- 14) W. H. Brattain and H. B. Briggs: Phys. Rev. **75** (1949) 705. T. S. Moss: Photocon. in the Elements.
- 15) R. DeL. Kronig: Proc. Roy. Soc. A, **124** (1929) 409; Proc. Roy. Soc. A, **133** (1931) 255.
- 16) K. Ishiguro and G. Kuwabara: *Method of Optical Measurement*, Series of Modern Physics (Iwanami Press, 1955) (in Japanese).
- 17) S. Nanba: Private Communication (at A. D. P. Committee Meeting).
- 18) G. Rupprecht: Z. Phys. **139** (1954) 504; A. Thelem and R. König: Naturwiss. **43** (1956) 297.
- 19) H. Dunnstädter: Z. Phys. **132** (1954) 383; G. Helwing: Z. Phys. **137** (1954) 401.
- 20) K. Akiyoshi and E. Kanai: Asahi Glass Company Research Repts. 8, no. 1 (1958).

- 21) Mochel: US Patent 2564706, US Patent 2564707.
- 22) I. Imai: to be published.
- 23) W. Shockley and J. Bardeen: Phys. Rev. **77** (1950) 407.
- 24) H. Y. Fan: Phys. Rev. **78** (1950) 808. T. Muto and S. Oyama: Progr. Theor. Phys. **5** (1950) 833 (Osaka).
- 25) A. Radowsky: Phys. Rev. **73** (1948) 749.
- 26) H. Y. Fan: Phys. Rev. **82** (1951) 900.
- 27) H. B. Callen: Phys. Rev. **76** (1949) 1394.
- 28) S. Serin: Phys. Rev. **70** (1946) 104. G. L. Pearson and J. Bardeen: Phys. Rev. **75** (1949) 865.
- 29) von Heywang: Z. Naturf. **4** (1949) 654. D. S. Saxon and R. A. Hutren: Philips Res. Rep. **4** (1949) 81.
- 30) J. Yamashita and T. Kurosawa: Private Communication.

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm × 7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 928

Screened Impurity Potentials in Metals

By E. C. McIrvine*

John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California

(Received February 4, 1960)

In a recent article¹⁾, Takimoto discusses the screening of an impurity potential by conduction electrons. The purpose of this note is to make some observations on the nature of the real-space potential which corresponds to this Fermi-Thomas treatment.

In the case of a degenerate electron gas (metal), one obtains a Fourier transform potential

$$U_{\kappa^0} = \frac{-4\pi Ze^2}{\kappa^2 + q^2 G(\kappa/2k_0)}, \quad (1)$$

where k_0 is the wave vector corresponding to the Fermi energy ζ , and

$$G(x) = \frac{1}{2} \left[1 + \frac{1}{2} \left(\frac{1}{x} - x \right) \log \left| \frac{1+x}{1-x} \right| \right]. \quad (2)$$

These expressions are contained in Eqs. (5.6) and (5.5) of Takimoto's paper.**

The Mott screening parameter²⁾ q is defined by

$$q^2 = \frac{6\pi n e^2}{\zeta}. \quad (3)$$

In the discussion which follows, it was found convenient to use in addition a "plasma screening" parameter q_p , defined by

$$q_p^2 = m\omega_p/\hbar, \quad (4)$$

where ω_p is the plasma frequency. This parameter, which appears to govern screening when $\zeta \ll \hbar\omega_p$, may also be expressed directly in terms of the Mott screening parameter by

$$\sqrt{3} q_p^2 = k_0 q. \quad (5)$$

The Fourier transform of Eq. (1) i. e. the potential in real space, may be obtained analytically in two special cases. For $\hbar\omega_p < 2\zeta$, ($q < \sqrt{3}k_0$), $G(x)$ may be expanded for small x , and the integration yields the real-space Mott potential²⁾

$$U(r_0) = -\frac{Ze^2}{r_0} \exp(-qr_0). \quad (6)$$

Only two terms of the expansion are retained, and

* Now at Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.

** A slight misprint in Eq. (5.5) has been corrected.

terms of the order of $q^2/12k_0^2$ are neglected. The potential is a simple screened potential, because $\kappa^2 + q^2 G(\kappa/2k_0)$ has pure imaginary zeros in this approximation.

For $\hbar\omega_p > 4\zeta$, ($q_p > \sqrt{2}k_0$), $G(x)$ may be expanded in x^{-1} . Even with the retention of only the first term, the zeros of $\kappa^2 + q^2 G(\kappa/2k_0)$ are now complex, and the resulting potential has an oscillatory nature in addition to screening characterized by q_p :

$$U(r_0) = -\frac{Ze^2}{r_0} \cos q_p r_0 \exp(-q_p r_0). \quad (7)$$

The appearance of an oscillating, but exponentially screened, potential will be characteristic of the general real-space solution of the Fermi-Thomas problem since, in the integration, complex exponentials are introduced by complex poles. Purely exponential screening can occur only if all the poles are pure imaginary. Purely oscillatory behavior^{3),4)} cannot result from the Fermi-Thomas treatment, since this would require negative $G(x)$ and real poles.

It is interesting to note that for copper, the Fermi energy from specific heat data is 4.8 eV. The calculated plasma frequency gives $\hbar\omega_p = 9$ eV; characteristic energy losses in copper occur at 20 eV. If the characteristic energy losses are due to plasma oscillations, then for copper $\hbar\omega_p = 4.2\zeta$. Even if the calculated value is correct, $\hbar\omega_p = 1.9\zeta$. Clearly, the condition for Mott screening is not well satisfied. Although the extreme potential given by Eq. (7) does not apply rigorously, it is probably as close to the truth as is Eq. (6). The actual potential for any metal will certainly contain some oscillatory behavior of the nature discussed, and will be dominated by exponential screening with a parameter given roughly by the smaller of the two screening parameters q and q_p .

I wish to acknowledge an interesting conversation with Dr. A. D. Brailsford, who has independently considered this problem.

References

- 1) N. Takimoto: J. Phys. Soc. Japan **14** (1959) 1142.
- 2) N. F. Mott: Proc. Cambridge Phil. Soc. **32** (1936) 281.
- 3) J. Friedel: Nuovo Cimento Suppl. **7** (1958) 287.
- 4) A. Blandin, E. Daniel and J. Friedel: Phil. Mag. **4** (1959) 180.

J. PHYS. SOC. JAPAN **15** (1960) 929

Magnetic Anisotropy Induced by Cold Rolling of Cu-Co Alloy

By Tadayasu MITUI

Department of Physics, Faculty of Science,
University of Hokkaido, Sapporo, Japan

(Received February 17, 1960)

The study was made for the purpose of making clear an origin of ferromagnetic anisotropy induced by cold rolling on the various precipitation processes of Cu-Co alloy containing ca. 2wt.% Co. Specimens were prepared from electrolytic copper of 99.9% purity and electrolytic cobalt of 99.8% in a Tammann furnace. After melting in crucibles, ingots were homogenized at ca. 1000°C and machined into disks with 10 mm in diameter and 4 mm in thickness. The disks were given a solid solution treatment consisting of a 2 hours anneal in vacuum at 1000°C followed by quenching into water. Subsequent 750°C-aging was done in vacuum and followed by water quenching.

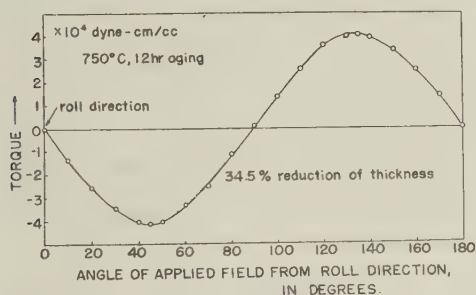


Fig. 1. Torque curve showing anisotropy produced by 34.5%-thickness reduction by cold rolling, measured in magnetic field of ca. 10 K Oe at 300°K.

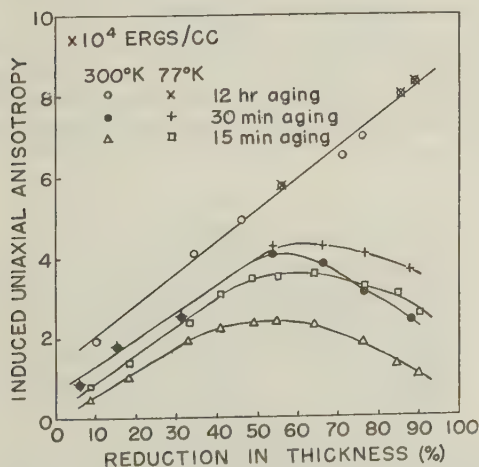


Fig. 2. Magnetic anisotropy vs thickness reduction for various aged states of 2% Co-Cu alloy.

Cold rolling on the aged specimens was done at room temperature without annealing. Determination of the induced anisotropy was made by means of the torque magnetometer. Specimens for this were cut into disk form from the rolled plane. The disks were prepared by successive rolling and shaping for the purpose of measuring the torque as a function of thickness reduction. The size of the disks was 10 mm in diameter and 4~0.4 mm in thickness.

The rolling produced a uniaxial magnetic anisotropy with the easy direction alloy the roll direction as shown in Fig. 1. The effect of changing the precipitation process on the anisotropy-thickness reduction curve is shown Fig. 2.

From these results, two significant features are to be seen. First, the anisotropy in the over-aged state is found to be the same at both 77°K and 300°K. This is a strong evidence for the shape anisotropy relating the shape change of the precipitates to the plastic deformation of the specimen. Secondly, the anisotropy as a function of the amount of reduction in thickness increases at first, and then, in the severely rolled states, decreases gradually as the mean size of precipitates decreases. This is interpreted in terms of the shape changes resulting from the cutting-off of precipitates by inhomogeneous slip. It is also concluded that the temperature dependence of the anisotropy is due to superparamagnetic effect resulting from the decrease in size of precipitates through cutting-off. Such a superparamagnetic effect in Cu-Co alloy was also demonstrated by Weil¹⁾. Satô and the author²⁾ found the decrease of coercivities induced by severe rolling in this alloy. On the other hand, Becker and Livingston³⁾ and Jan⁴⁾ have concluded for Cu-Co alloy and for Al-Ag and Al-Zn alloys respectively that the plastic deformation in these alloys takes place by zones of homogeneous fine slip rather than large amounts of glide in a limited number of glide planes. However, their conclusion would be unlikely to explain our result for the heavy deformation.

Accordingly, we do wish to point out that the relative magnitude of the size of precipitates and the glide distance of slip is important for the purpose of using a precipitation phenomenon as a tool to study a mechanism of slip.

The detailed report will be published in this Journal.

References

- 1) L. Weil: J. phys. radium **20** (1959) 289.
- 2) M. Satô and T. Mitui: Phys. Soc. Japan **14** (1959) 1254.
- 3) J. D. Livingston and J. J. Becker: Trans. Amer. Inst. Mech. Engrs. **212** (1958) 316.
- 4) J. P. Jan: J. Appl. Phys. **26** (1955) 1291.

J. PHYS. SOC. JAPAN **15** (1960) 930

On the Alpha-particles from the $N^{14}(d, \alpha)C^{12}$ Ground State Reaction

By Nawoyuki KAWAI

Department of Physics, Faculty of Science,
Kyushu University, Fukuoka, Japan

(Received February 22, 1960)

Angular distributions of the alpha-particles from the $N^{14}(d, \alpha)C^{12}$ ground state reaction were measured in the energy range of deuterons from 1.4 to 2.9 MeV. This preliminary measurement was performed together with the investigation on the $N^{14}(d, p)N^{15}$ reaction and the details of experimental procedures will be described in the report on this reaction¹.

The deuteron beam from the electrostatic generator was collimated with a silver slit of 4 mm in diameter and then was incident upon a target placed at the center of a scattering chamber. The target used was melamine ($C_3H_6N_6$) evaporated on a silver backing in vacuum and the thickness of melamine was measured to be 0.3 mg/cm². The emitted alpha-particles, after passing through apertures of 6 mm in diameter bored at intervals of 15° at the side wall of the scattering chamber and sealed with 20 μ thick aluminium foils, were detected with an 1 mm thick CsI(Tl) crystal and a

photomultiplier. Pulses from the detector were fed to a linear amplifier and analyzed with a twenty channel pulse height analyzer.

In the pulse height distributions observed at each angle, the peak corresponding to the alpha-particles from $N^{14}(d, \alpha)C^{12}$ ground state reaction was assigned by the reaction kinematics. This peak was clearly separated from the proton groups from the $N^{14}(d, p)N^{15}$ and $C^{12}(d, p)C^{13}$ reactions in the angular range from 15° to 105°. But, at angles larger than 105°, the alpha-particles were masked by the above mentioned proton groups and so angular distributions were measured only in the range below this angle. In Fig. 1, observed angular distributions are shown. Absolute values of the differential cross sections were evaluated by comparing them with that of the $C^{12}(d, p)C^{13}$ ground state reaction² and so the absolute scales of ordinates in Fig. 1 were expected to have an uncertainty of factor 2.

In the energy range of deuterons investigated, a general feature of angular distributions is a forward peak and considerably rapid decrease down to a minimum at about 80°. Beyond this minimum, it increases again rather gradually. These results are consistent with that of Booth *et al.* at deuteron energy below 1 MeV³) and of Gibson *et al.* at 8 MeV⁴). It will be interesting to notice that these angular distributions are considered to show asymmetry about 90°, although the measurement is confined only in the range below 105°. From this fact, it may be concluded that, even in such a lower energy region of deuterons as in the present experiment, the $N^{14}(d, \alpha)C^{12}$ ground state reaction still proceeds not only by the compound nucleus process, but also by the direct interaction, probably the pick-up process pointed out by Fischer *et al.* at the higher energy region⁵).

More detailed experiments on this reaction are now in progress in our laboratory.

The author wishes to express his cordial thanks to Prof. I. Nonaka, Dr. M. Morita and all other staffs of the nuclear laboratory of Kyushu University for their support and discussions throughout this work.

References

- 1) To be published in J. Phys. Soc. Japan.
- 2) M. T. McEllistrem, K. W. Jones, Ren Chiba, R. A. Douglas, D. F. Herring and E. A. Silverstein: Phys. Rev. **104** (1956) 1008.
- 3) D. L. Booth, F. U. Price, D. Roaf and G. L. Salmon: Proc. Phys. Soc. London **A**, **71** (1958) 325.
- 4) W. M. Gibson and E. E. Thomas: Proc. Roy. Soc. **A**, **210** (1951) 543.
- 5) G. E. Fischer and V. K. Fischer: Phys. Rev. **114** (1959) 533.

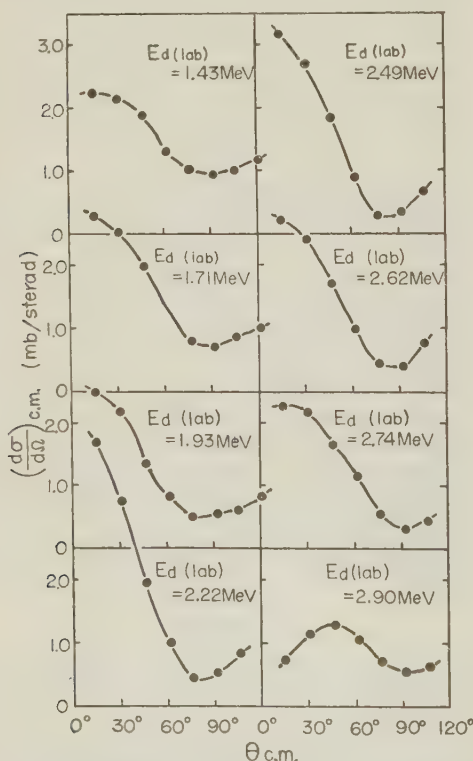


Fig. 1. Angular distributions of the alpha-particles from the $N^{14}(d, \alpha)C^{12}$ ground state reaction.

J. PHYS. SOC. JAPAN **15** (1960) 931**Ferromagnetism of Mn-Zn Alloy**By Seiji TEZUKA, Sukeyoshi SAKAI
and Yasuaki NAKAGAWA*Department of Physics and Chemistry,
Gakushuin University,
Mejiro, Tokyo*

(Received March 3, 1960)

Nowotny and Bittner¹⁾ have briefly reported that Mn-Zn alloys containing about 30 at.% Mn are ferromagnetic at room temperature if quenched from high temperatures. According to Schramm²⁾ the high-temperature phase (ϵ -phase) has the c.p.h. lattice, while the low-temperature phase (α -phase) is f.c.c. in the range 25-30 at.% Mn. The present authors have found that the ferromagnetism of these alloys is due to the existence of a metastable phase which is c.p.h. probably with superlattice structure.

The specimens containing 27 at.% Mn were prepared by melting Mn and Zn sealed together in evacuated quartz tubes. After homogenized at 550°C the specimens were quenched into water. The Debye-Scherrer photograph shows only c.p.h. lines ($a=2.75 \text{ \AA}$, $c/a=1.61$), and the magnetization of the same specimens is not large at room temperature. It is remarkable, however, that the magnetization becomes much larger if the quenched specimens are annealed at rather low temperatures.

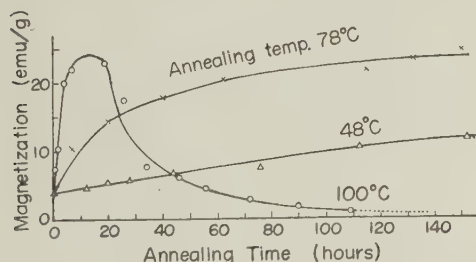


Fig. 1. Magnetization at room temperature in magnetic field of 7000 Oe, plotted against annealing time.

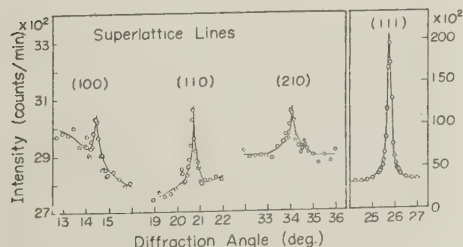


Fig. 2. X-ray diffraction intensities for α' -phase, measured by stop-counting method using Fe K_{α} radiation.

Fig. 1 shows the room-temperature values of magnetization plotted against the annealing times, the annealing temperatures being 100°C, 78°C and 48°C. As can be seen in the figure, the ferromagnetic phase is merely metastable.

The Debye-Scherrer photograph of the specimen which has the largest value of magnetization shows distinct c.p.h. lines together with faint f.c.c. lines, while that of the specimen annealed at 100°C for several hundred hours shows only f.c.c. lines ($a=3.87 \text{ \AA}$). Since the atomic numbers of Mn and Zn are not very different, the superlattice lines cannot be detected in the Debye-Scherrer photographs. By using an X-ray diffractometer, however, the superlattice in the f.c.c. phase (α' -phase) has been confirmed, as shown in Fig. 2. The calculated intensities based on the Cu_3Au -type (Ll_2 -type) structure are in rough agreement with the experimental values. It is very likely that also the metastable ferromagnetic c.p.h. phase has the superlattice structure (D0_{19} -type), although the direct confirmation has not yet been made. This phase is referred to as ϵ' -phase. It can be concluded from the above results that the transformation caused by the low-temperature annealing is as $\epsilon \rightarrow \epsilon' \rightarrow \alpha'$. The $\epsilon \rightarrow \epsilon'$ transformation requires diffusion of atoms, whereas the $\epsilon' \rightarrow \alpha'$ transformation requires only the change in stacking order of the atomic planes normal to the c -axis of the c.p.h. lattice.

It has also been found that the α' -phase becomes ferromagnetic at 140°K. The ferromagnetic Curie point of the ϵ' -phase, on the other hand, is evidently higher than 400°K. In both the ϵ' - and α' -phases of MnZn_3 , each Mn atom is surrounded by six Mn atoms at a distance of $3.87 \text{ \AA}$. The remarkable difference in Curie point between the two phases may thus be due to the next-near-neighbour interaction; the next-near-neighbour distances between Mn atoms are $4.42 \text{ \AA}$ and $5.47 \text{ \AA}$ in the ϵ' - and α' -phases, respectively. The details of this work will be published later together with the studies on the Mn-Zn alloys with other compositions.

References

- 1) H. Nowotny and H. Bittner: *Monatsh. Chemie* **81** (1950) 887.
- 2) J. Schramm: *Z. Metallkunde* **32** (1940) 399.

J. PHYS. SOC. JAPAN **15** (1960) 932**Ferrimagnetism of Mn_3Ge_2**

By Kō YASUKŌCHI, Kazuo KANEMATSU

*Department of Physics,
College of Science and Engineering,
Nihon University, Tokyo*

and Tetuo OHYAMA

*Department of Physics, Faculty of Science,
Tokyo Metropolitan University*

(Received March 4, 1960)

Recently, in the course of our study on the magnetic properties of intermetallic compounds in Mn-Ge system, we have confirmed that Mn_3Ge_3 and Mn_3Ge_2 are ferromagnetic and parasitic ferromagnetic respectively, as were reported by Fakidov et al.¹⁾ and found $\text{Mn}_{3.25}\text{Ge}$ to be antiferromagnetic in its disordered state²⁾.

In the present note will be reported, the temperature dependence of the magnetic property of Mn_3Ge_2 (28.6 at.% Ge) measured by a pendulum magnetometer and a magnetic balance as well as a ferrimagnetic behavior found in its low temperature phase. The specimen of the compound used in the experiment was prepared as follows; powders of electrolytic manganese (99.9%) and germanium (seven-nine purity) were mixed at the desired proportion, Mn : Ge = 5 : 2, and the mixture was sealed in a evacuated quartz tube, melted by an electric furnace at 1150°C, and quenched into water at

750°C, and then annealed at 500°C for three days and quenched again into water. The absolute values of the saturation magnetization of the compound are plotted against temperature in Fig. 1, curve I, and the inverse values of its magnetic susceptibilities over 700°K are also shown in the same figure, curve III. With increasing temperature from 90°K, first, the saturation magnetization decreased monotonically and disappeared at 395°K. Then it began to grow again, and finally, after it reached a maximum value at 630°K, declined quite rapidly toward zero at 710°K. The occurrence of magnetization curve of this kind was suggested as *N*-type by Néel in his theory of ferrimagnetism³⁾, and first reported experimentally for Li-Cr-ferrite by Gorter and Schulkes⁴⁾. According to Néel's theory, in the *N*-type ferrimagnetism, the spontaneous magnetization changes sign at a certain temperature, "compensation" point. Then, in order to ascertain the reversal of the spontaneous magnetization in our specimen, a simple demonstration was carried out as in the following; a rod of this material was magnetized and suspended torsion-free in a small magnetic field ($< H_c$), and on heating or cooling through 395°K, the reversal of the direction of the rod was confirmed apparently. It is seen by this result that the spontaneous magnetization indeed changes its sign at that temperature, curve II.

Thus the intermetallic compound, the low temperature phase of Mn_3Ge_2 , may be considered as a typical *N*-type ferrimagnetic material with Néel point of 710°K and compensation point of 395°K. This conclusion is also supported by the fact that curve III is concave against the temperature axis. The examination with X-ray diffractometer to determine the crystal structure of Mn_3Ge_2 is now in progress. The details will be published later.

The authors wish to express their hearty thanks to Prof. S. Kaya, the President of Tokyo University, for his constant encouragement and are also very grateful to Profs. Y. Tomono and S. Iida of Tokyo University who gave them facilities to achieve the work.

References

- 1) I. G. Fakidov and Yu. N. Tsiovkin: FMM. **7** (1959) 685.
- 2) K. Yasukōchi, T. Ohoyama and K. Kanematsu: J. Phys. Soc. Japan **14** (1959) 1820.
- 3) L. Néel: Ann. physique **3** (1948) 137.
- 4) E. W. Gorter and J. A. Schulkes: Phys. Rev. **90** (1953) 487.

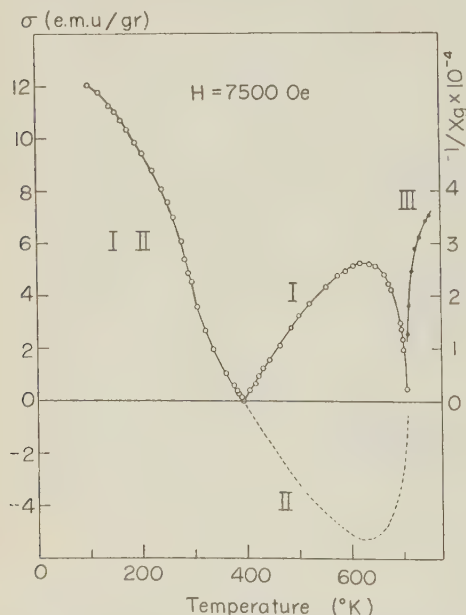


Fig. 1. I. Saturation magnetization of the low temperature phase of Mn_3Ge_2 vs temperature. II. Spontaneous magnetization. III. Inverse susceptibility vs temperature.

Spin Order in the Doublet at the Second
Excited level in Even-even
Medium Nuclei

By Mitsuo SAKAI

*Institute for Nuclear Study, University of
Tokyo, Tanashi-machi, Tokyo*

(Received March 1, 1960)

Accumulation of experimental data in the last decade appears to increase the significance of the presence of two spin levels, 2+ and 4+, in a close doublet at about twice the energy of the first excited level in even-even medium nuclei¹⁾. Especially the recent experiments on the Coulomb excitation by McGowan and Stelson²⁾ have shown in many nuclei the presence of 2+ level close to the known second 4+ level. In this paper, we call this pair of levels as a doublet. So many such nuclei have been found that it is very attractive to believe the presence of the doublet at the second excited level as a general feature of the even-even medium nuclei. In order to make sure such a view, it is desirable to find more example of such a nucleus by the help of some guiding rules, either experimental or theoretical. It is just for this purpose that in a recent article³⁾ we have discussed the appearance of these spin levels from the point of view of beta decay selection rules.

In this note we present systematics of the spin order of 2+ and 4+ level in the doublet, which may help us to predict the position of the unknown partner of the doublet. All the even-even nuclei, which are known up to the present to have the doublet, are included in Fig. 1, in which $\epsilon_1(4)/\epsilon_2(2)$ is plotted against $\epsilon_2(2)/\epsilon_1(2)$, $\epsilon_1(4)$, $\epsilon_2(2)$ and $\epsilon_1(2)$

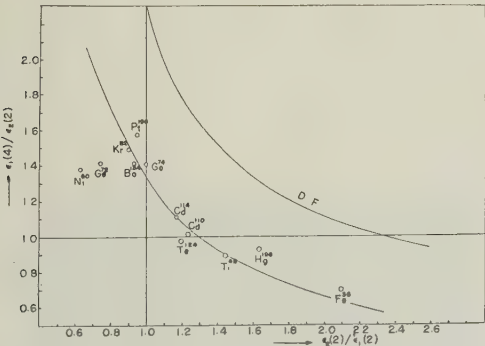


Fig. 1. Plot of $E_1(4)/E_2(2)$ vs $E_2(2)/E_1(2)$. The curve denoted D. F. is the theoretical curve from Davidov and Filippov's paper⁴⁾. Two exceptional isotopes Ni⁶⁰ and Ge⁷² may be explained by the magic number $Z=28$ for the former isotope and the sub-magic number $N=40$ for the latter isotope.

being the gamma ray energies defined in Fig. 2. It is rather surprising that the points are found nearly on a smooth curve. Therefore, if we have a known 2+ level, we can easily predict from this diagram the position of the unknown 4+ level by using the known ratio of $\epsilon_2(2)/\epsilon_1(2)$. It can be concluded also from this figure that in the nuclei having $\epsilon_2(2)/\epsilon_1(2) \leq 1.3$, the upper level in the doublet should be 4+.

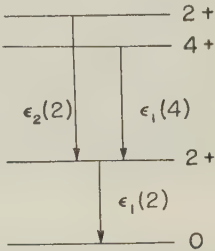


Fig. 2. Schematic presentation of low lying level system in even-even medium nuclei.

The curve expected from the asymmetric rotor theory⁴⁾, which has had a remarkable success in explaining almost all experimental data on nuclear properties throughout the nuclear chart, is also drawn in Fig. 1. Although this and the empirical curve are nearly parallel, a large discrepancy can be noticed. This situation is just contrary to that in the heavy nuclei, of which the points are found nearly on this theoretical curve. These findings may be correlated to the facts that the ratio $\epsilon_1(4)/\epsilon_1(2)$ is 1.3 and 2.3 for the medium nuclei and for the heavy nuclei, respectively, as pointed out by Mallmann⁵⁾ and that the 4+ level in the nuclei having a smaller $\epsilon_1(4)/\epsilon_1(2)$ value than 1.3 has no 2+ level partner.

The author wishes to thank Messrs. H. Ikegami and T. Yamazaki for the helpful discussions.

References

- 1) K. Way et al.: Ann. Rev. Nucl. Sci. **6** (1956) 129.
- 2) P. H. Stelson and F. K. McGowan: Bull. of Amer. Phys. Soc. **2** (1957) 267.
- 3) M. Sakai: Institute for Nuclear Study Report INS-J **19** July (1959).
- 4) C. Marty: Nucl. Phys. **1** (1956) 85; Nucl. Phys. **3** (1957) 193. A. Davydov and G. Filippov: Nucl. Physics **8** (1958) 237. D. M. Van Patter: Nucl. Physics **14** (1959) 42.
- 5) C. A. Mallmann: Phys. Rev. Letters **2** (1959) 507.

J. PHYS. SOC. JAPAN 15 (1960) 934

On the $F \rightarrow F'$ Conversion in the Presence of A -, M -, R - and Z_1 -Centers

By Hiroshi OHKURA, Katsunobu AWANE
and Shigeko MIYAMOTO

Department of Applied Physics,
Osaka City University, Osaka

(Received March 24, 1960)

The decrease of the optical quantum efficiency for the $F \rightarrow F'$ conversion in potassium chloride crystals in the presence of A -, M -, R - and Z_1 -centers was investigated.

Single crystals of potassium chloride made by careful repetitions of Kyropoulos method were colored additively. To introduce Z_1 -centers the crystals were doped previously with a small amount of strontium chloride. Optical absorption measurements and F -light irradiations were made with the help of the Hitachi EPU-2 type spectrophotometer. All measurements of optical absorption were made at liquid air temperature.

The successive decreases of the F -absorption peak due to the $F \rightarrow F'$ conversion caused by the successive irradiation with F -light at $-100^\circ \pm 3^\circ\text{C}$ were measured. The F -light we used was $520\text{ m}\mu$ in wave-length and $5\text{ m}\mu$ in band pass. The decreases of F -center density ΔN_F were calculated assuming the oscillator strength to be 0.8. The ratios of ΔN_F against initial density N_{F_0} were plotted as functions of irradiation time as shown as curve 1 in Fig. 1.

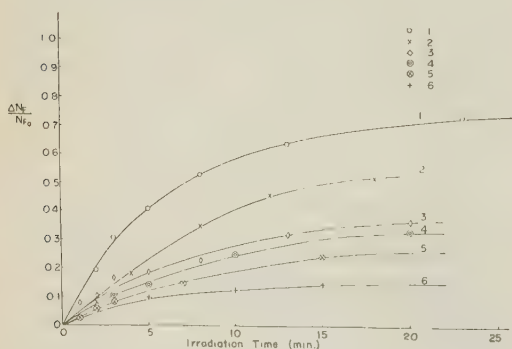


Fig. 1. The successive decreases of F -center density versus irradiation time at -100°C . The ordinate is the ratio of the decrease of F -center density against initial F -center density in each run.

Curve 1: pure F -center ($N_{F_0} = 1.7 \times 10^{16} \text{ 1/cc}$),
Curve 2: F and A ,
Curve 3: F , A and M ,
Curve 4: F , A , M and R ,
Curve 5: F , A , M and R ,
Curve 6: F , M and R .

The results of the same measurements carried out in the presence of A -, M - and R -centers which had been converted previously from F -centers under irradiation with F -light at room temperature were shown as curves 2, 3, 4, 5, 6 in Fig. 1. The wave-length used to irradiate at room temperature was $550\text{ m}\mu$ with band pass of $30\text{ m}\mu$. The same plots for strontium-doped and colored potassium chloride crystals are shown in Fig. 2 for the various concentrations of Z_1 -centers.

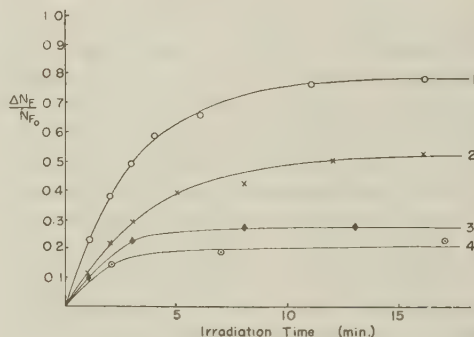


Fig. 2. The successive decreases of F -center density versus irradiation time at -100°C . The ordinate is the ratio of decrease of F -center density against initial F -center density in each run.

Curve 1: pure F -centers ($N_{F_0} = 2.7 \times 10^{16} \text{ 1/cc}$),

Curve 2: F , A and Z_1 ,

Curve 3: F , Z_1 ,

Curve 4: F , Z_1 .

These experimental results clearly show that both the initial speeds of $F \rightarrow F'$ conversion (which correspond to optical quantum efficiencies) and the saturated values of $\Delta N_F / N_{F_0}$ are considerably reduced by the presence of A -, M -, R - and Z_1 -centers. Although these facts can be qualitatively interpreted in terms of enhancement of the trapping probability of photo-electrons due to the presence of complex (impurity) centers and newly increased negative ion vacancies by F -bleaching, which acts to decrease the probability of $F \rightarrow F'$ conversion, the details of investigation will give some insight into the structure of complex centers, the mechanism of creating processes of these centers and the role of negative ion vacancies.

Authors wish to express their thanks to Professor H. Kawamura for giving us his whole-hearted guidance in the course of this work.

This work was supported by the Scientific Research Fund of Ministry of Education.

J. PHYS. SOC. JAPAN **15** (1960) 935

Observation of Microplasma Pulses and Electroluminescence in Gallium Phosphide Single Crystal

By Makoto KIKUCHI and Takashi IIZUKA

Electrotechnical Laboratory, Tokyo, Japan

(Received March 9, 1960)

Microplasma pulse noise similar to those observed in Si *p-n* junction and silver-paste electrode on Si has been found in reverse-biased point contact electrode on gallium phosphide single crystal. Single crystals of GaP were prepared in quartz ampoule mixing 10 to 20% of phosphorus in Ga. Single crystals of about 3 mm in diameter were formed after careful heat treatment.

Typical reverse voltage-current characteristic of tungsten point contact on GaP is shown in Fig. 1. Pulse noise, as shown in Fig. 2, which is quite similar to those observed in Si *p-n* junction, appears at point A and disappears as the bias voltage is increased up to point B. In the case of Fig. 2, pulse height was about 7 micro-amp. at the bias

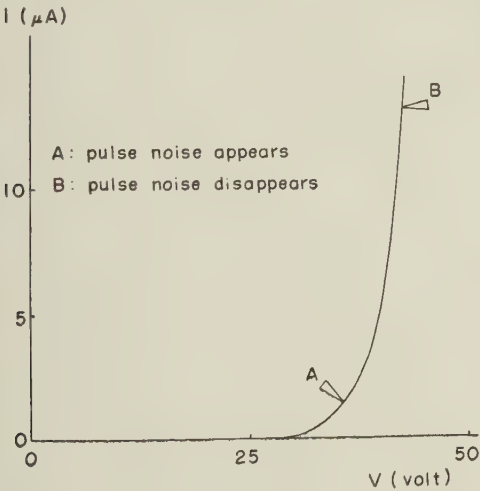


Fig. 1. Reverse characteristic of point contact on Gap.

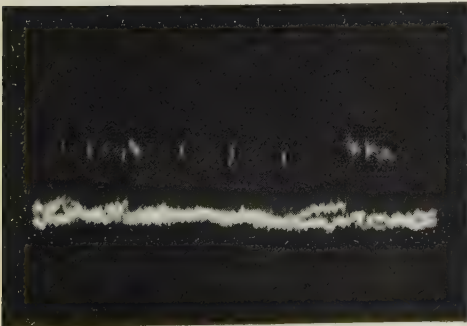
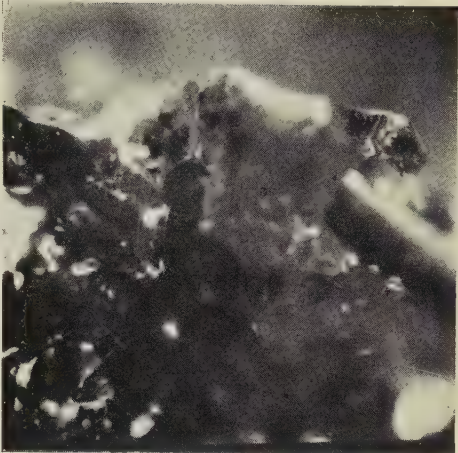
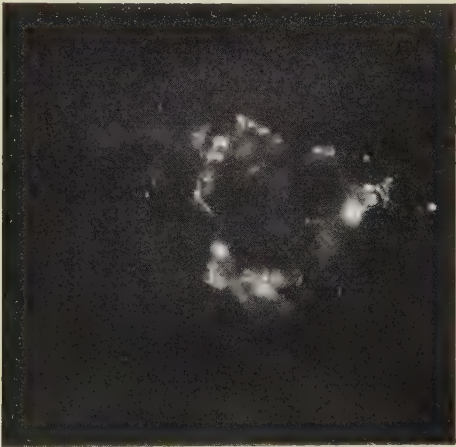


Fig. 2. Microplasma pulse noise in point contact on Gap.



(a)



(b)

Fig. 3. (a) Photomicrograph of point contact on Gap and (b) electroluminescence.

voltage slightly above point A. In general, it was much more difficult to catch clear pattern of microplasma pulses on the synchroscope than in the case of Si *p-n* junction because of high level of current noise, which might partly be attributed to the choice of tungsten needle for metal electrode. The pulse width ranged from 1 to 20 microseconds near the bias point of its appearance.

Electroluminescence was observed as shown in Fig. 3(b). By careful observation, it seemed likely that the true light-emitting spot was located just beneath the point contact, as can be seen in Fig. 3, and other bright spots were only reflections of the light emitted from it.

In our samples, without intentional doping, no electroluminescence could be observed in the forward bias either by naked eyes or through microscope. It must also be noted that no photoelectric effect could be detected with the light from a projector lamp.

Magnetic Annealing of Co and Co-Ni Alloys

By Minoru TAKAHASHI and Tatsuo KōNo
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai
(Received February 29, 1960)

For several years, the present author has studied the magnetic behavior of various ferromagnetic alloys under isothermal magnetic annealing at high temperatures, in order to elucidate the origin of the magnetic annealing effect, and has obtained

some results which are not expected from the theory of atomic pair orientation¹⁾. The present report concerns the magnetic annealing effect of polycrystalline pure Co and Co-Ni alloys with the phase transition $\gamma \rightarrow \epsilon$.

To prepare the specimens, Inco electrolytic nickel and Katango electrolytic cobalt were used. The results of chemical analysis are given in Table I. The specimen shape was a circular disc, 12.8 mm in diameter and 0.45 mm in thickness. The torque measurement was carried out by a usual torque-magnetometer, and the field strength for the measurement was 2250 Oe. The torque values were obtained both from the specimens annealed with magnetic field of 410 Oe and from those annealed

Table I. Results of chemical analysis of metals used.

Metal	Fe (%)	Co (%)	Ni (%)	C (%)	Mn (%)	Si (%)	Al (%)	P (%)	S (%)	Cu (%)
Electrolytic Ni	0.01 ₇	0.16	—	0.00 ₈	trace	0.00 ₅	—	trace	trace	0.00 ₄
Electrolytic Co	0.04 ₁	—	0.34	0.00 ₉	trace	0.00 ₅	trace	0.00 ₂	trace	—

without magnetic field. The difference of these values gave the induced magnetic anisotropy. Examples of the torque curve are shown in Fig. 1. As seen from this figure, the shape of the curves is represented by $\sin 2\theta$, in which θ is the angle between the direction of intrinsic magnetization

and that of the applied field in the cooling, and hence the amplitude of the curves should give K_u , which is the constant of uniaxial anisotropy. For nickel-rich Co-Ni alloys without phase transition, the torque is the same order in magnitude as that of Ni-Fe alloys. For cobalt-rich Co-Ni alloys, on the other hand, it is extremely large, and it should be noted that even pure cobalt has the uniaxial anisotropy. The field direction in the magnetic cooling is parallel to the axis of easy magnetiza-

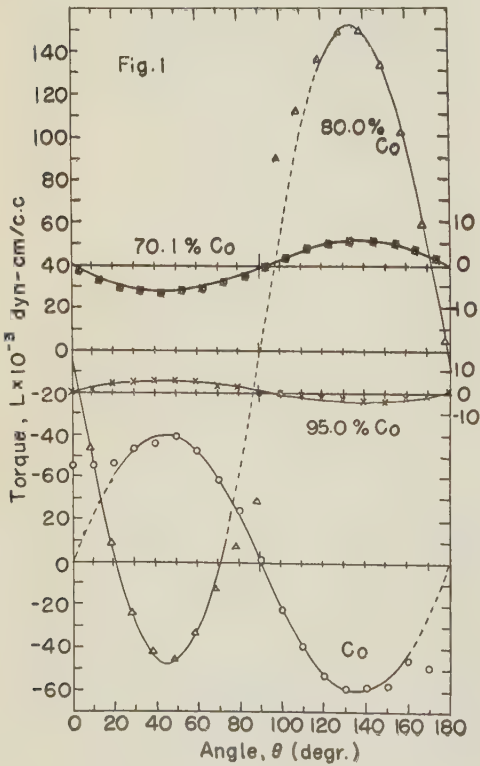


Fig. 1.

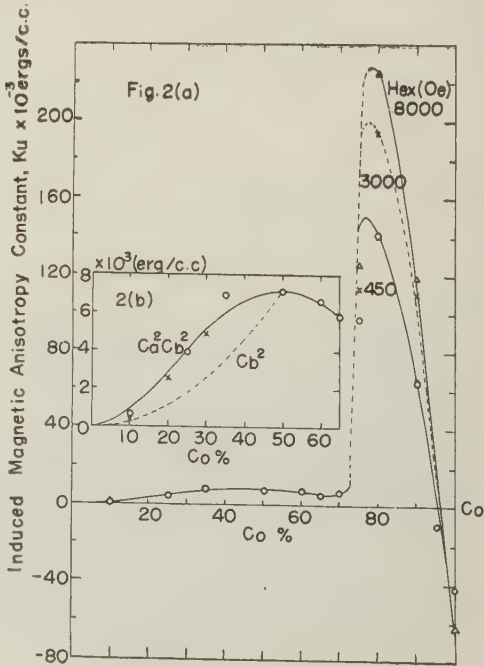


Fig. 2(a), 2(b).

tion except in pure cobalt and 95% Co-Ni alloy, while in these cases it is parallel to the axis of difficult magnetization, as seen in Fig. 1. The value of K_u was plotted as a function of concentration of cobalt in Fig. 2(a). The γ -phase region of this figure is magnified in Fig. 2(b), where the curve can approximately be expressed by $C_a^2 C_b^2$, provided that C_a and C_b are concentrations of Ni and Co, respectively. K_u is very large in the ε phase region and depends on the field strength in the magnetic cooling. The maximum value, 23.0×10^4 ergs/cc, was obtained at about 80% Co-Ni alloy, while the value is -6.0×10^4 ergs/cc for pure cobalt. These large values of $|K_u|$ seem to be closely connected with the $\gamma \rightarrow \varepsilon$ phase transition. The detailed report will be published in the near future.

References

1) L. Néel: *Compt. rend.* **237** (1953) 1613; *J. phys. radium* **15** (1954) 225. S. Taniguchi: *Sci. Rep. Res. Inst. Tohoku Univ.* **A**, **7** (1955) 269. S. Chikazumi and T. Omura: *J. Phys. Soc. Japan* **10** (1955) 842. S. Chikazumi: *J. Phys. Soc. Japan* **11** (1956) 551.

J. PHYS. SOC. JAPAN **15** (1960) 937~938

Electrical Properties of Stannic Oxide Films

By Isamu IMAI

Department of Physics,
College of General Educations,
University of Tokyo

(Received February 24, 1960)

We have already reported some results derived from optical and electrical properties of stannic oxide films at room temperature¹⁾. In the present paper the temperature dependence of the electrical properties of this substance was measured in order to obtain another support of the previously reported conclusions.

The specimens used in these measurements were prepared on the fused quartz plates by the same method as the previous experiment¹⁾. Since the irreversible changes occur when the temperature of the specimen is raised above $\sim 200^\circ\text{C}$ in vacuum, we have measured the conductivity σ , Hall constant R_H and Seebeck effect $d\theta/dT$ in the region between the room and liquid nitrogen temperatures, where these effects are reproducible. (Fig. 1) The existence of ohmic law in the electrical properties of the specimens was always confirmed because they were polycrystalline thin films.

From Fig. 1, we recognize that both σ and R_H

increase slightly with temperature. But as there is the doubt that this effects might be due to the difference between thermal expansion coefficients of the film and the substrate, the electrical properties of the specimen prepared on the soda glass at the same time with the specimen Sn42 were also measured. Since the results show the same characteristics, it is concluded that these behaviours are intrinsic of the stannic oxide film.

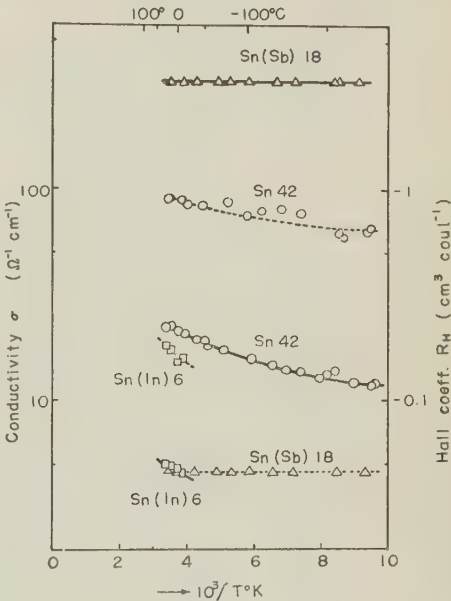


Fig. 1. — σ vs. $1/T$ and --- R_H vs. $1/T$.
Specimen Sn42 was prepared by spraying alcohol solution of pure SnCl_4 on the fused quartz substrate. Specimens Sn(Sb)18 and Sn(In)6 were obtained by spraying solutions $\text{SnCl}_4 + 1 \text{ mol\% SbCl}_5$ and $\text{SnCl}_4 + 3 \text{ mol\% InCl}_3$ respectively.

As is seen from the fact in Fig. 1 that σ and R_H do not change appreciably with temperature and $d\theta/dT$ has small values, it is expected that these substances are in considerably degenerate states. It is due to this fact that stannic oxide films show metallic conduction. We have applied the free electron theory to analyze the experimental data, though the Seebeck effect is not usually used so much for it. In the procedure, we first made an attempt to estimate the expected value of the Seebeck effect from R_H and appropriately adopted effective mass value m^* of free carrier by using the relations

$$n = 1/R_H e, \quad n = 4\pi(2m^*kT/\hbar^2)^{3/2} F_{1/2}(\xi)$$

and

$$\frac{d\theta}{dT} = -\frac{k}{e} \{ (p+5)F_{3/2}(\xi) / (p+3)F_{1/2}(\xi) - \xi \},$$

where p is scattering index defined from the proportionality of relaxation time τ to v^p and $F_j(\xi)$ is

Fermi integral, the value of which was obtained graphically. Assuming $m^*=m/7$, which is the value obtained from optical and electrical measurements in the previous work¹⁾, the expected values of $d\theta/dT$ are shown in Table I. It may be seen from the table that the agreement between the experimental and calculated values of $d\theta/dT$ is better in the case $p=3$ than $p=-1$. This implies that the free carriers are largely scattered by ionized centers.

Table I. $d\theta/dT(\mu V/\text{deg.})$

	300°K			100°K		
	$p=3$	$p=-1$	exp.	$p=3$	$p=-1$	exp.
Sn42	193	82	145	54	19	50
Sn(Sb)18	32	11	38	11	3.6	14
Sn(In)6	78	28	80	—	—	—

On the other hand, there are some facts that are compatible with this conclusion as follows: (1) If we calculate from Fig. 1 the difference of the carrier densities between the specimen Sn(Sb)18 and Sn42, we shall find it nearly equal to the added density of Sb, indicating that Sb seems to act as a donor. Since a donor will be positively charged after supplying a free electron, as is seen from the R_H values in Fig. 1 the ionized impurity density in the specimen becomes so high that impurity scattering will be more important than lattice scattering in the conduction mechanism. (2) The mobilities $\mu_H=R_H\sigma$ obtained from Fig. 1 increase with the temperature in the specimens except Sn(Sb)18, which is independent of temperature on account of high degree of degeneracy. Their exponents on temperature dependence are approximately +1, while it should be +3/2 in pure $p=3$ case and -3/2 in $p=-1$.

In conclusion, conversely if $p=3$ in the specimens is valid by the reasons mentioned above, the present measurements seem to support that the ratio of the effective free electron mass to the true electron mass is about 1/7, whose value have been observed in the previous work¹⁾.

Reference

- 1) K. Ishiguro, T. Sasaki, T. Arai and I. Imai: J. Phys. Soc. Japan **13** (1958) 296.

J. PHYS. SOC. JAPAN **15** (1960) 938~939

Post-Irradiation Effect in Visible Absorption Spectra of Polyvinyl Chloride Sheets

By Yoichi OKADA, Takao ITO

Research Institute,
Sumitomo Bakelite Co. Ltd., Tokyo

and Ayao AMEMIYA

Department of Applied Physics,
Faculty of Engineering,
University of Tokyo, Tokyo

(Received March 2, 1960)

We applied visible absorption spectrophotometry to irradiated sheets of polyvinyl chloride so as to obtain some information about mechanism for post-irradiation effect and color change with time.

Irradiation was done with electron beams (energy 1 MeV, current 100 μ A). Samples of polyvinyl chloride sheets 1 mm in thickness, 5 cm $\times$ 3 cm in size, contained only a kind of organic tin as stabilizer so that they were optically transparent. They were irradiated up to dose 10^8 rad or 10^7 rad, some were irradiated in water and others in air.

The spectra were measured by means of a Simazu-QB-50 type unit. In particular, we traced the absorption change with time after irradiation for about 24 hours. We could not measure a color change in the samples irradiated up to 10^8 rad because of its too strong absorption. All the subsequent discussions therefore refer to the samples irradiated up to 10^7 rad only.

Visual color gradually changed from blue to green after irradiation. An example of absorption spectrum is shown in Fig. 1.

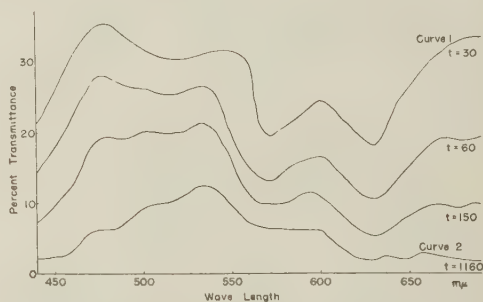


Fig. 1. Absorption spectra of a sample irradiated in water. Curve 1 and Curve 2 refer to measurements at 30 min and 1160 min, after irradiation.

As shown in Fig. 1, two absorption bands (at 570 μ and 630 μ) were observed. Although one might be tempted to think that the change in color means a shift of the bands, but they did not shift with time. Consequently, visual change in color above mentioned is due to a certain gradual distortion of a spectral shape. We calculated color specification according to the CIE standard system from the spectra in Fig. 1. For curve 1, $\lambda_d=500$ μ (bluish green), $p_e=7\%$ and $Y=26.83$; for curve 2, $\lambda_d=541$ μ (yellowish green), $p_e=36\%$ and $Y=7.20$, where λ_d , p_e , and Y represent dominant wavelength, excitation purity and illuminous refractance respectively. These values are consistent with our

visual observations.

The value of $\log(I_0/I)$ at the absorption bands is plotted against time in Fig. 2, where I stands for the intensity of transmission of an irradiated sample and I_0 for that of an unirradiated sample.

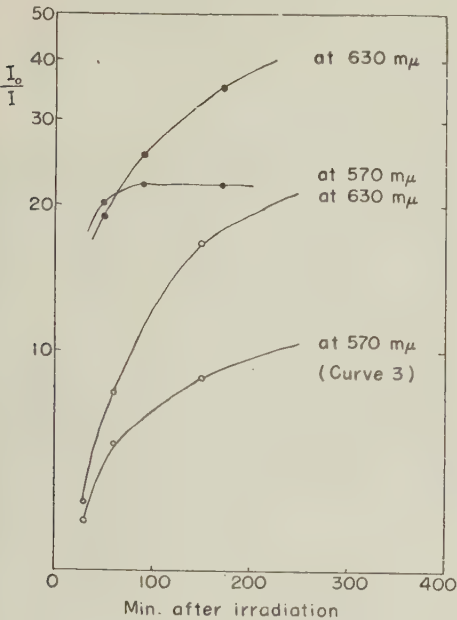


Fig. 2. $\log(I_0/I)$ at absorption bands.
○: Irradiated in water.
●: Irradiated in air.

A possible interpretation of our present result is given as follows. The primary product due to irradiation may be a metastable species without visible absorption. This species may then convert itself secondarily to a chromophore responsible for the absorption band above mentioned. The conversion process will be supposed to be unimolecular, at least apparently. The secondary product, or the chromophore, may be considered to be a stable species because of its constancy at the absorption wavelength.

From the first order reaction kinetics, the next functional relationship may be applied to the curve in Fig. 2.

$$\gamma = \gamma_0 + \gamma_1 [1 - \exp(-\lambda t)] .$$

Here, γ represents $\log(I_0/I)$ at time t and γ_0 that at time $t=0$. t represents time after irradiation. γ_1 and λ are constants to be determined independent of time. γ_1 is connected with γ_0 by the equation, where γ_∞ is $\log(I_0/I)$ at time $t \rightarrow \infty$.

$$\gamma_\infty = \gamma_0 + \gamma_1 .$$

Evidently γ is proportional to concentration of the chromophore. If we adjust the parameters as $\gamma_0 = 0.35$, $\gamma_1 = 0.61$ and $\lambda = 2.2 \times 10^{-2} \text{ min}^{-1}$; the above equation can reproduce the curve 3 in Fig. 2, approximately, so that the half life of the primary

product turns out to be 32 min.
More detailed study is now in progress.

J. PHYS. SOC. JAPAN **15** (1960) 939~940

Interaction Effects in $\text{K}_3\text{Fe}(\text{CN})_6$

By Taiichiro OHTSUKA
*The Research Institute for Iron,
Steel and Other Metals,
Tôhoku University*
(Received March 3, 1960)

The electron configuration of the Fe^{3+} ion in $[\text{Fe}(\text{CN})_6]^{3-}$ complex is $(d\epsilon)^5$. A cubic field gives a ground orbital triplet which is split further by the combined action of the spin-orbit interaction and fields of lower symmetry¹⁾. The ground level may be described by an effective spin $S'=1/2$.²⁾ Because the orbital momentum is only partially quenched there is a possibility of anisotropic exchange³⁾. A detailed measurement by McKim and Wolf⁴⁾ of the Weiss constants in a single crystal has shown the existence of a rather large anisotropic component. The anomalously large line breadth of the paramagnetic resonance line in a concentrated salt has been interpreted as due to this anisotropic exchange⁵⁾.

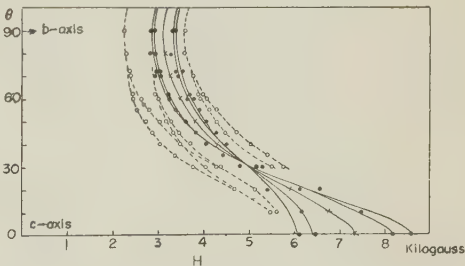


Fig. 1. Position of lines in bc -plane. —●— Solid line calculated using values of anisotropic exchange listed in Table I and with c -axis as the z -axis; —×— isolated ion line, $g_0=2.18$, $g_c=0.92$; ---○--- dotted line drawn through experimental points.

We have observed paramagnetic resonance in samples diluted by $\text{K}_3\text{Co}(\text{CN})_6$. At about 5% Fe^{3+} concentration a fine structure consisting of many lines are observed which have intensities of about one tenth of the line due to isolated ions. Fig. 1 shows the angular dependence of these lines in the bc -plane. The lines can be separated into those which are situated approximately symmetrically about the isolated ion line (points joined by a solid line) and those which are not (points joined by

dotted line). The origin of the latter lines are not clear at the moment. We shall present here a brief report on the analysis of only the former lines as these appear to have a close connection with the anisotropic component of the Weiss constant.

According to Barkhatov and Zhdanov⁶⁾ the crystal is monoclinic with two differently oriented complexes per unit cell. The relevant parameters are listed in Table II. The magnetic axes coincide with the crystal axes. The former lines appear to be due to exchange coupled pairs of similarly oriented ions from the behavior in the *ab*-plane and reasons to be given later. With $S'=1/2$ the ions combine to give a total spin $T=1$ or 0. It has been shown that the anisotropic component of exchange splits the triplet and gives rise to a pair of lines situated approximately about the non-displaced positions⁷⁾. The lines can be analysed with the following Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot (\mathbf{S}' + \mathbf{S}'') + \mathbf{S}'\mathbf{K}\mathbf{S}'' \quad (1)$$

The angular dependence of the lines indicate that the principal axes of the exchange interaction tensor lie along the crystal axes. Hence the principal values of the anisotropic component will be denoted by J_a , J_b and J_c where a , b and c denote the crystal axes. Now besides the anisotropic exchange, dipolar interaction between ions also contributes to the splitting of the triplet. In the present case this amounts to about 20% of the anisotropic exchange and cannot be neglected. The contribution will depend on the sign of the anisotropic exchange and the orientation of ion pairs. The factors were taken so as the resulting values of J_a etc. after correction for the dipole effect satisfied the condition $J_a + J_b + J_c = 0$. This determines the sign of J_a etc. and also shows that the lines are most probably due to pairs of similar ions. For all alternative cases there arises a 10% discrepancy between $J_a + J_b$ and the observed J_c . The values thus derived are shown in Table I. It is not clear from the crystal structure why there should be two different similar ion pairs. When the number of nearest neighbours are taken to be $n=2$, the anisotropic Weiss constant gives values listed in the last row of Table I.

It is seen that they agree very well in both magnitude and sign with the average of the two pairs. This is another reason why we believe the lines to be due to similar ion pairs as $n=4$ for dissimilar ions. McKim and Wolf have also noted that a fair agreement between the Weiss constant and the magnetic specific heat could be obtained only when one assumes $n=2$ instead of $n=6$ as suggested from the crystal structure. Although the reason is not clear these facts are consistent with each other and can be understood if we assume that the anisotropic component of the inter-

Table I.

	J_a (cm ⁻¹)	J_b (cm ⁻¹)	J_c (cm ⁻¹)
Pair I	-.038	-.016	+.055
Pair II	-.047	-.025	+.072
Average of I & II	-.043	-.021	+.064
From Weiss const. ⁴⁾ with assumption of $n=2$	-.044	-.024	+.067

Table II. Crystal parameters for $K_3Fe(CN)_6$.

a (Å)	b (Å)	c (Å)	β	Z
7.05	10.44	8.40	107.5	2
Fe at 000; $\frac{1}{2}\frac{1}{2}0$				

action between dissimilar ions is very small.

We have also made adiabatic demagnetization measurements on a single crystal of concentrated salt with hope of obtaining more information on the isotropic exchange. There appears a peak in the susceptibility at the entropy $S/R=0.165$. Using the Weiss constants this is calculated to be about 0.2°K. An independent experimental determination of the absolute temperature is being made. These results will be reported together with a detailed discussion of the resonance results in a forthcoming paper.

The author expresses his thanks to Prof. E. Kanda for his encouragement throughout the course of this work.

References

- 1) J. B. Howard: J. Chem. Phys. **3** (1935) 813. H. Kamimura: J. Phys. Soc. Japan **11** (1956) 1171.
- 2) B. Bleaney and M. O'Brien: Proc. Phys. Soc. London **B**, **69** (1956) 1216.
- 3) B. R. Judd: Proc. Roy. Soc. **A**, **250** (1959) 110.
- 4) F. R. McKim and W. P. Wolf: Proc. Phys. Soc. London **B**, **69** (1956) 1231.
- 5) J. M. Baker, B. Bleaney and K. D. Bowers: Proc. Phys. Soc. **B**, **69** (1956) 1205.
- 6) V. Barkhatov and H. Zhdanov: Acta Phys.-Chim. URSS **16** (1942) 43; rf. Structure Report vol. **9**, 209.
- 7) J. M. Baker and B. Bleaney: Conf. Phys. Bases Temperatures 1955. Griffiths, et al. Proc. Roy. Soc. **A**, **250** (1959) 84.

J. PHYS. SOC. JAPAN **15** (1960) 941~942

Temperature Dependence of Infrared Absorption Bands of *n*-Higher Alcohols

By Mitugi HASIKUNI

Department of Physics, Faculty of Science,
Hiroshima University

(Received March 2, 1960)

The temperature dependence of infrared absorption bands of *n*-higher alcohols was examined in the range from 700 cm^{-1} to 1500 cm^{-1} . It was found that the intensities of some of the bands changed markedly with temperature. When the sample was heated from room temperature (20°C), each of the bands which are characteristic of the solid state became gradually fainter and finally disappeared at a certain temperature which was different from band to band. When the sample is cooled down from the liquid state, the bands begin to reappear at temperatures which are lower by several degrees than those corresponding to the heating process.

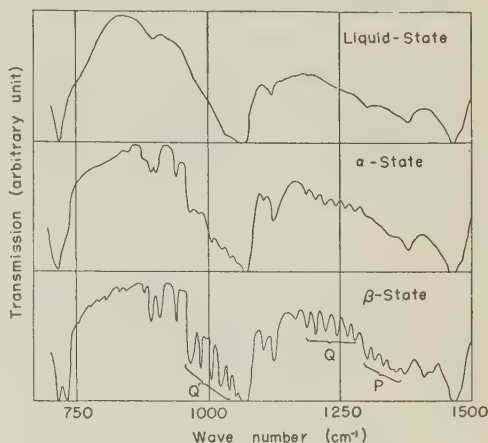
In the spectra on the β -states, three progressions of bands (*P*, *Q* and *Q'* in Fig. 1) were observed. These bands are characterized by uniformity of relative intensity and spacing, and by the same dependence on temperature.

Fig. 1 shows the absorption curves for $\text{C}_{18}\text{H}_{37}\text{OH}$, $\text{C}_{16}\text{H}_{33}\text{OH}$, and $\text{C}_{14}\text{H}_{29}\text{OH}$ in the liquid, α - and β -states, respectively. Though the spectra of the liquids agree well with the spectrogram reported by N. Neuilly¹⁾, the spectra of the β -states reveal more structure than that observed by him. However, the spectra do not confirm the fact that the bands between 1350 cm^{-1} and 1180 cm^{-1} (*P* and *Q* in Fig. 1) consist of two overlapping series of bands as mentioned by R. N. Jones, A. F. McKay and R. G. Sinclair²⁾. Nevertheless, these bands can be classified into two groups by their temperature dependence, the group between 1250 cm^{-1} and 1350 cm^{-1} (*P* group in Fig. 1) and the group between 1180 cm^{-1} and 1250 cm^{-1} (*Q* group in Fig. 1).

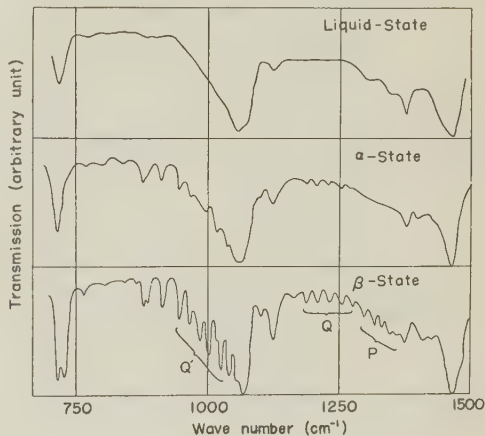
In the case of cooling process from the liquid state to solid state, the *Q* and *Q'* (bands between 1048 cm^{-1} and 964 cm^{-1}) groups begin to appear when the specimen freezes. Next, the *P* group appear at somewhat lower temperature. Finally, the doublet at 720 cm^{-1} begins to split at the transition temperature for α - β modification. All the bands which appear only in the solid state are gradually intensified as the temperature becomes lower.

The fact that no abrupt change in the intensity of the spectra occurs in the process of passing through the liquid- α and α - β transition points is

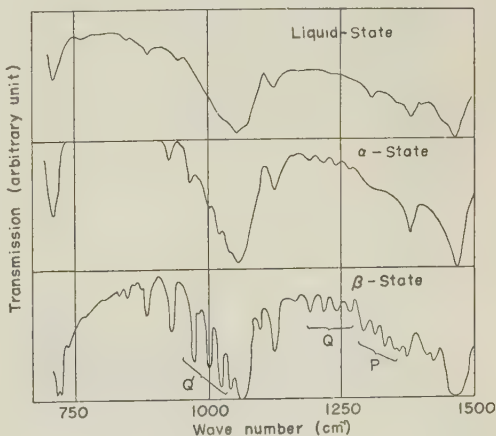
the primary difference between the spectral properties and other properties such as electrical con-



(a)



(b)



(c)

Fig. 1. Infrared spectra of *n*-higher alcohols in three states.

(a) $\text{C}_{18}\text{H}_{37}\text{OH}$ (b) $\text{C}_{16}\text{H}_{33}\text{OH}$ (c) $\text{C}_{14}\text{H}_{29}\text{OH}$

ductivity or dielectric loss which change abruptly at these temperatures³).

A detailed description will be published later.

References

- 1) N. Neuilly: *Compt. rend.* **238** (1954) 65.
- 2) R. N. Jones, A. F. McKay and R. G. Sinclair: *J. Amer. Chem. Soc.* **74** (1952) 2575.
- 3) M. Takeyama: *J. Sci. Hiroshima Uni. A*, **21** (1957) 219.

J. PHYS. SOC. JAPAN **15** (1960) 942~943

Stress in Very Thin Vacuum-Evaporated Films of Silver

By Koreo KINOSITA, Hideki KONDO
and Ichiro SAWAMURA

*Department of Physics and Chemistry,
Gakushuin University, Mejiro, Tokyo*

(Received March 5, 1960)

In recent years the stress in vacuum-evaporated films has aroused the interest of the workers in thin film physics, and not a few papers have been published on this subject*. It seems, however, that no systematic study has yet been carried out on the relation between the magnitude of the stress and the thickness of the film. The authors have measured the tensile stress in silver films of 30~2,500 Å thickness evaporated *in vacuo* on thin pieces of mica, and obtained the results illustrated in Fig. 1.

The substrate, a thin piece of mica (3~5 cm in length, 0.4~0.8 cm in width and 0.001~0.005 cm in

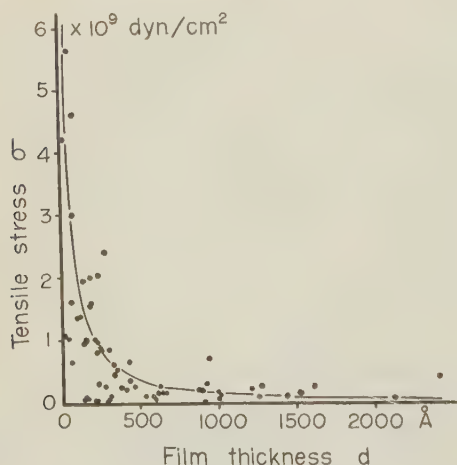


Fig. 1. Relation between stress and film thickness.

* These works have been reviewed by Kondo and Kinoshita¹).

thickness), was clamped on to a copper block as is shown in Fig. 2. This block was mounted horizontally in a bell-jar and silver was evaporated from a molybdenum boat placed 40 cm below the block. The evaporation was carried out at $1\sim3 \times 10^{-5}$ mmHg, the speed being between 20 and 40 Å/sec.

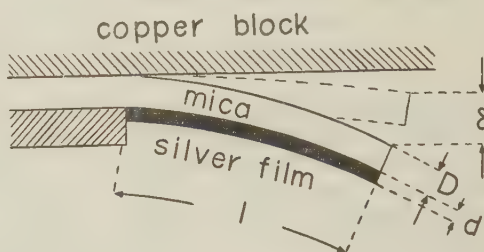


Fig. 2. Mica piece and its support. Before and after evaporation.

The displacement of the free end of the mica piece was observed through a window of the bell-jar by means of a horizontal microscope equipped with an ocular micrometer. During the evaporation the mica piece shows a free-end-up deformation due to thermal effect, but when the evaporation is finished and the thermal equilibrium is reached, the free end comes to a standstill after being shifted downward by an amount δ (0.001~0.05 cm). This displacement is caused by the tensile stress σ in the silver film. It can be shown that

$$\delta = 3l^2 d \sigma / E D^2,$$

where E and D are the Young's modulus and the thickness of the substrate, and l and d are the length and the thickness of the silver film respectively. E was determined for each substrate by the method of vibrating reed²). The thickness of the silver film, d , was measured making use of the multiple-beam Fizeau fringe technique.

Fig. 1 indicates that above 500 Å film thickness (the region which have been studied hitherto) σ increases slightly as d decreases. But below 500 Å σ increases steeply as d decreases, by far exceeding the tensile strength of bulk silver (1.6×10^9 dyn/cm²). It would be worthy of note that the σ - d relation given in Fig. 1 resembles that between the electric resistivity and the thickness of the evaporated silver film³).

The general trend of the σ - d curve suggests that the stress is concentrated in a surface layer of the evaporated film. This view would be more favourable to Wilman's theory⁴) than to Hoffman's⁵).

It seems that the sharp rise in σ below 500 Å is beyond the scope of any existing theories. It is substantial to know more about the structure of these thin films before any theory for the cause of the stress in this region can be proposed. The

authors have started electron microscopic observation of very thin ($d < 100 \text{ \AA}$) films of silver evaporated on mica under the same conditions as described above. The micrographs obtained up to the present show agglomerated structures, but there is strong evidence that agglomeration is accelerated by the electron beam. The authors are rather inclined to suppose that evaporated silver atoms form a continuous film on freshly cleaved mica surface, which by irradiation with the electron beam or by aging may be metamorphosed into an agglomerated structure.

References

- 1) H. Kondo and K. Kinoshita: J. Appl. Phys. Japan **28** (1959) 553 (in Japanese).
- 2) See e.g. F. Kohlrausch: *Praktische Physik* (Teubner, Leipzig und Berlin, 1935), S. 94.
- 3) See e.g. U. Oppenheim and J. H. Jaffe: J. Appl. Phys. **24** (1953) 1521.
- 4) H. P. Murbach and H. Wilman: Proc. Phys. Soc. London **B**, **66** (1953) 905, etc.
- 5) H. S. Story and R. W. Hoffman: Proc. Phys. Soc. London **B**, **70** (1957) 950, etc.

J. PHYS. SOC. JAPAN **15** (1960) 943~944

Electron Spin Resonance in Irradiated Polytetrafluoroethylene: Decomposition of the Complex Spectrum

By Naoyuki TAMURA

Tokyo Laboratories, Japanese Association for Radiation Research on Polymers,
Komagome-Kamifujimae,
Bunkyo-ku, Tokyo,
Japan

(Received March 11, 1960)

Spectrum of electron spin resonance in irradiated pure polytetrafluoroethylene (PTFE) has been reported by Rexroad and Gordy to consist of two quintets, partially superimposed, arising from radicals of the form of $-\text{CF}_2\dot{\text{C}}\text{FCF}_2-^{1)}$. We have also been investigating the ESR of irradiated PTFE, and observed some new phenomena.

Measurements were made at a frequency of 9400 Mc/sec with a reflection-type apparatus (JES ESR spectrometer). Irradiation was carried out at room temperature with γ -rays from a 1000-curie ^{60}Co source giving a dose rate of $3.4 \times 10^5 \text{ r/hr}$. PTFE samples in the form of rod, 3 mm in diameter, having a crystallinity of approximately 60% were irradiated in glass tubes, after degassing and sealing in vacuum, with dose of up to $6 \times 10^7 \text{ r}$.

Integrated curve of derivative tracing of spectrum obtained at 27°C is given by curve *S* in Fig. 1(a). This spectrum cannot be explained by two quintets with an intensity distribution of 1:4:6:4:1. Though the intensity of the spectrum hardly decays at room temperature, it varies with elevation of the temperature as shown in Fig. 2, the heating time of the sample being 3 min. at each temperature. Two principal decay regions are observed, the first arose in the $70\text{--}100^\circ\text{C}$ region and the second above about 180°C . The polymer lost its spectrum entirely on heating at 320°C . Since in PTEE the segmental motion in the amorphous regions occurs at about $100^\circ\text{C}^{2)}$ and the crystalline regions melt at 327°C , the radical decays observed

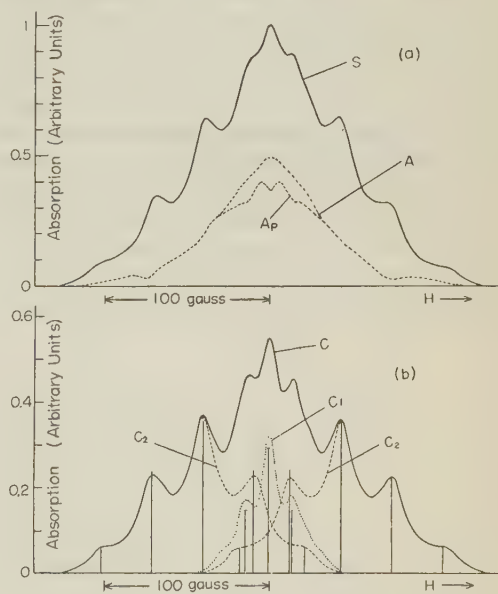


Fig. 1. Integrated curve of derivative tracing of spectrum at 27°C for PTFE. (a) Initial spectrum, *S*, and the part of the spectrum which disappeared on heating at 130°C , *A*. (b) Spectrum which remained on heating at 170°C , *C*, and its decomposition into two components *C*₁ and *C*₂.

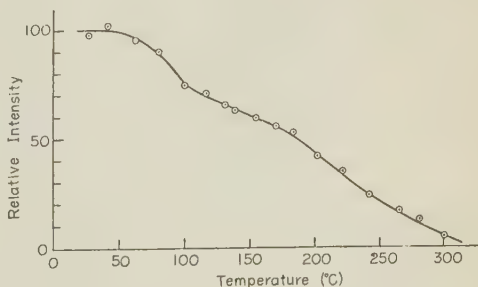


Fig. 2. Relative intensity of spectrum as a function of heating temperature for PTFE.

seem to correlate with the chain motion of the polymer.

After the first decay region the spectral intensity decreases to about 60% of its initial value, showing that the radicals in the amorphous regions decay first. This spectrum which disappeared consists of several overlapping lines smeared out as shown by curve *A* in Fig. 1(a), which is obtained by subtracting the spectrum resulting from heating at 130°C from the original curve *S*. The partial conversion of *A* into *C*₁ (Fig. 1(b)) also occurs, so the actual curve of *A* should be obtained by adding this converted part to the apparently disappeared line *A*_p.

On heating at 170°C, spectrum shown by curve *C* in Fig. 1(b) was obtained. This spectrum can probably be attributed to radicals produced in the crystalline regions. The spectrum may be resolved into two components *C*₁ and *C*₂, the former being composed of three narrow lines and the latter of two quintets with but slight difference in *g*-factors (about 0.001). The relative intensity of five lines is approximately 1:4:6:4:1, and that of three lines, 1:2:1. The vertical bars drawn directly

below the curves represent the theoretical intensity. The curve *C*₂ is thought to arise from the radical with five coupling fluorines—one with coupling of 87 gauss and four with equivalent couplings of 32 gauss each. The curve *C*₁ is to be attributed to the second radical in the crystalline regions with hyperfine intervals of 14 gauss. On heating at 280°C, the curve *C*₁ disappears completely leaving curve *C*₂ of diminished intensity.

Thus the complex spectrum of irradiated PTFE may be explained by superposition of curves *A*, *C*₁ and *C*₂ originating from at least three different kinds of radicals.

The author is deeply indebted to Dr. Kenichi Shinohara for his encouragement and interest in this work. He is also grateful to Mr. T. Matsugashita for his helpful discussion.

References

- 1) H. N. Rexroad and W. Gordy: J. Chem. Phys. **30** (1959) 399.
- 2) K. H. Illers and E. Jenckel: Kolloid-Z. **160** (1958) 97. N. G. McCrum: J. Polymer Sci. **34** (1959) 355.

Errata

Theory of Viscoelasticity of Amorphous Polymers, II. A Note on the Time-Temperature Reducibility of the Relaxation and Retardation Spectra

By Osamu NAKADA

J. Phys. Soc. Japan **12** (1957) 1218

Eq. (40), which we had derived as the condition for the microscopic reducibility, should be revised partly as follows. The solution of Eq. (32) with $F_e = F_0 \delta(t)$ is expressed formally

$$f_1(q, t) = e^{-tL} f_1(q, 0), \quad t \geq 0. \quad (E-1)$$

While, the direct integration of Eq. (32) in the neighborhood of $t=0$ leads to

$$f_1(q, 0) = -F_0 \operatorname{div} (f_0/\xi). \quad (E-2)$$

Thus

$$f_1(q, t) = -e^{-tL} F_0 \operatorname{div} (f_0/\xi). \quad (E-3)$$

Accordingly the conditions for f_1 to be described in the form of Eqs. (23) and (24) should be Eq. (40) and

$$f_0(q, T)/\xi(T) = \lambda(T) f_0(q, T_0)/\xi(T_0), \quad (E-4)$$

the latter of which we had missed in the original text. The equilibrium distribution function f_0 depends on temperature through Boltzmann's factor except when the potential energy of the system is everywhere constant in the configuration space, i.e., except when the component L_i equals zero. But as we see easily considering Eq. (40) together with Eqs. (33), (34), (35) and (36), the condition that L_i should be zero is already involved in Eq. (40). So our conclusion previously derived will not be altered ultimately by inclusion of the supplementary condition (E-4). The author should like to express his sincere thanks to Mr. K. Okano of the Institute of Physical and Chemical Research who pointed out the mistake.

Measures of Finite Strain and Stress-Strain Relations

By Wataru SEGAWA

J. Phys. Soc. Japan **15** (1960) 518

Page	Column	Line		Should be read
518	left	28	and i4 not	and is not
519	left	9	$g_{ij} - g'^{\lambda\mu}$	$\delta_{\lambda\mu} - g'_{\lambda\mu}$
519	left	36	g_{ii}	g_{ii}
519	left	42	$e_{13}^L e_{13}^L$	$e_{31}^L e_{13}^L$
519	right	10	e^{ii}	e_{ii}
519	right	29	definition.	definitions,
520	left	42	$(\partial x^{*k})_{,j} x_{,j}^{*k}$	$(\partial x^{*k})_{,j} x_{,i}^{*k}$
520	left	43	δx^{**}	$\delta x^{*\alpha}$
520	right	4	$\delta(x_{,j}^{*k}) = (\gamma x^{*k})_{,i}$	$\delta(x_{,i}^{*k}) = (\delta x^{*k})_{,i}$
521	left	4	$\partial A / \partial I_L$	$\partial A / \partial I_L'$
521	left	14	above	as above
521	right	40	tree	three

PROGRESS OF THEORETICAL PHYSICS

CONTENTS

Progress of Theoretical Physics	Vol. 23, No. 3, March 1960
Thermodynamic Functions of the Relativistic Thomas-Fermi Atom at Low Temperature.....	Vishnu S. MATHUR..391
Diamagnetism of Electrons in a Weak Periodic Potential.....	Robert M. MAY..400
Green Function Method for Electron Gas. I— <i>General Formulation</i> —	
.....	H. KANAZAWA and M. WATABE..408
Green Function Method for Electron Gas. II— <i>Dispersion Relation of Plasmons</i> —	H. KANAZAWA, S. MISAWA and E. FUJITA..426
Green Function Method for Electron Gas. III— <i>Diamagnetism</i> —	
.....	H. KANAZAWA and N. MATSUDAIRA..433
Electron Pairs in the Theory of Superconductivity	John M. BLATT..447
Bose Einstein Condensation of Correlated Pairs...T. MATSUBARA and J. M. BLATT..	451
On the Vibration of Disordered Linear Lattice. III	Jun-ichi HORI..475
S-Wave Pion-Nucleon Scattering	K. KAWARABAYASI and H. MIYAZAWA..490
Relativistic Rotators and Bilocal Theory	
.....	D. BOHM, P. HILLION, T. TAKABAYASI and J. P. VIGIER..496
Stopping Power of High Temperature Plasma— <i>Effects of Ionic Collective Motion</i> —.....	Yoshi H. ICHIKAWA..512
Letters to the Editor:	
S-Wave Pion-Nucleon Interaction and Nucleon Core.....	Shigeo MINAMI..519
On the Eigenvalue Problem Associated with the Solution of General-ized Diffusion Equation	Akira MIYAKE..521
On the Test of Global Symmetry	T. SAKUMA and S. FURUI..522
Nonlocal Interaction, Causality and Integrability Condition	
.....	Yoshio MIYATAKE..524
On the Extremum Property in the Variation Principle in the Theory of Transport Processes	Huzio NAKANO..526
On the Extremum Problem in the Variation Principle in the Theory of Susceptibility or Relaxation Phenomena	Huzio NAKANO..527
Contents of Journ. Phys. Soc. of Japan, Vol. 15, No. 2	i-ii

Price \$ 1.25 per copy
\$ 15.00 per year (postage inclusive)
Annual dues for foreign members (individual subscribers)
\$ 12.00 (postage inclusive)
" for foreign members of the Physical Society of Japan
\$ 10.00 (postage inclusive)
Application for members, subscriptions and orders for back numbers should be sent, directly or through book-dealers, to
The Publication Office
in
Yukawa Hall, Kyoto University, Kyoto, Japan
.....

Further Study of the Reaction ${}^7\text{Li}(\gamma t){}^4\text{He}$

By Mitsuo MIWA and Mikio YAMANOUCHI

Department of Physics, Tokyo University of Education, Tokyo

(Received February 2, 1960)

The reaction ${}^7\text{Li}(\gamma t){}^4\text{He}$ is studied by using betatron bremsstrahlung and nuclear emulsion. Resonance peaks are found in the excitation function at 7.8, 8.9, 9.8 and 13.5 Mev, in agreement with those found previously by one of the authors (Miwa). From the angular distribution analysis, it is concluded that the spin and the parity of the 8.9 Mev level in ${}^7\text{Li}$ is $5/2^+$.

§ 1. Introduction

In the former work¹⁾ (hereafter referred to as I), one of the authors (Miwa) investigated the excitation function of the reaction ${}^7\text{Li}(\gamma t){}^4\text{He}$ up to the x -ray energy of 21 Mev, finding peaks in the excitation curve at the photon energies of 7.6, 8.6, 9.6, 11.7, (13.5) and 16.2 Mev. A few of the peaks were found to correspond to the known excited levels of ${}^7\text{Li}$ nucleus. Some others, however, were somewhat uncertain and did not correspond to any known levels.

In the present work, we have tried to confirm the existence of the peaks observed in I by observing more events. Besides the energy distribution of the events, the angular distribution of reaction products has also been studied in order to make up for defects in determining the resonances only from apparent peaks in the cross section curves, because there may appear spurious peaks due to statistical fluctuation.

We have identified and established some of the peaks found in I, and where it was possible, we have tentatively assigned the spins of the corresponding levels of ${}^7\text{Li}$ nucleus.

§ 2. Experimental Procedure

Five nuclear plates have been examined. Three of which (Nos. 1, 2, and 3) were the plates exposed to the bremsstrahlung from the betatron at the University of Illinois, while the other two (Nos. 4 and 5) were those irradiated with the betatron at the Tokyo University of Education.

As was described in I, the plates Nos. 1, 2 and 3 were exposed to the x -ray beam with their surface normal to the beam. This arrangement had the advantage of reducing fogging in the emulsion. In this case, however, it was difficult to observe tracks with

angles larger than around 50° to the plate. Therefore the plates Nos. 4 and 5 were set with their surfaces at 10° to the beam. This setting was a compromise between reducing fogging and increasing observable angular range. 200-micron Ilford E1 plates loaded with lithium of 32 mg per cm^3 emulsion were used throughout the work.

The arrangement of experimental apparatus in exposing the plates Nos. 4 and 5 was nearly the same as in I. Nuclear plates were placed at the center of a long cadmium tube with its axis parallel to the x -ray beam to get rid of undesirable alpha-triton pairs arising from the reaction ${}^6\text{Li}(nt){}^4\text{He}$, and, in order to reduce the fogging of the emulsions to the same degree as in the case when the plate was placed normally to the beam, the bremsstrahlung was filtered by a tungsten plate of 4 mm thickness. The x -ray dose was measured by a Victoreen chamber encased in a paraffin cylinder of 20 cm diameter placed far behind the nuclear plate.

Table I.

Plate	No. 1	No. 2	No. 3	No. 4	No. 5
Betatron energy (Mev)	18	17	11	18	20
Given dose (roentgen)	200	260	140	220	220
Area scanned (cm^2)	5.6	4.6	3.8	2.9	3.0
Tracks measured	702	304	219	210	136

Table I shows the betatron energy and the dose given to each plate together with the area scanned and the number of tracks measured.

Irradiated plates were processed by the usual method of temperature development.

The developing agent was a modified normal amidol developer, pH value of which was 6.5 at 19°C. Satisfactory discrimination of alpha-triton pairs was achieved against background tracks and foggs.

The energy of the photon having produced each alpha-triton pair was determined from the observed range of the pair. Hence the struggling of alpha particles and tritons in the emulsion caused some ambiguity in determining the photon energy. In order to estimate the magnitude of the resultant uncertainty in the photon energy, the struggling of alpha particles was measured, by observing the ranges of alpha particles of samarium and polonium in Fuji ET2E plates. The measured struggling was in good agreement with that obtained by Rotblat²⁾ for Ilford C2 emulsion.

From these results, the uncertainty of the photon energy determined from the observed alpha particle energy was estimated to be less than ± 0.4 MeV at about 8 MeV photon energy. Triton tracks were expected to exhibit much less struggling. Finally, photon energies E_1 and E_2 for each pair were calculated from the observed ranges of its alpha and triton components respectively, and to make sure the pair identification, few pairs having $\varepsilon = (E_1 - E_2)/E_2$ greater than 0.07 were excluded from the data.

In studying the angular distribution, the tritons emitted between 40° and 140° with respect to the α -ray beam were measured for the plates Nos. 1, 2 and 3, and for the plates Nos. 4 and 5 only those tracks having dip angles less than 50° with respect to the surface of the plates were accepted for measurement. Necessary corrections for the limited observable angular range and for the escaping of the emitted particles from the emulsion in the case of the plates Nos. 4 and 5 were applied in a similar way to that of Wächter³⁾.

§ 3. Results and Discussion

Figs. 1(a), (b) and (c) represent energy distributions of the alpha-triton pairs which survived the criterion mentioned in the preceding section. Corresponding excitation functions are shown in Fig. 2. The result of I is reproduced in Fig. 2 for comparison. Although the absolute values of reaction cross

section are not in good accord in some cases, it may safely be said that the excitation functions in Fig. 2 obtained from different measurements show a marked similarity in their general trend. Absolute cross sections at the α -ray energy of 6.8 MeV obtained from the plates Nos. 4 and 5 are also indicated in Fig. 2. These values however are not expected to be quite accurate because of the

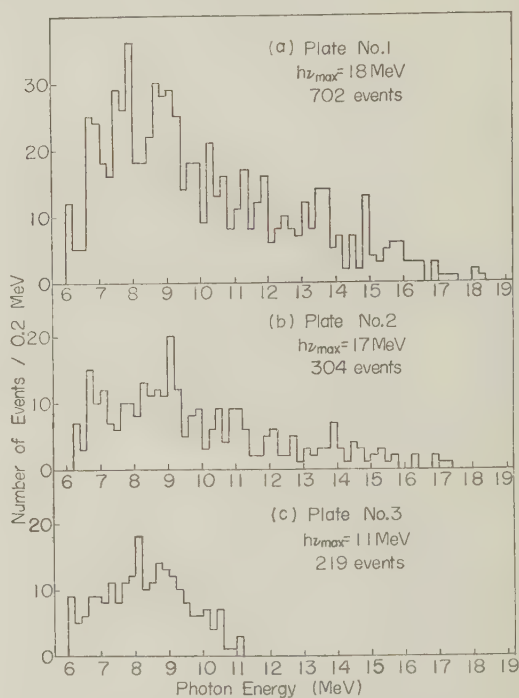


Fig. 1. Energy distribution of alpha-triton pairs from the reaction ${}^7\text{Li}(\gamma)t{}^4\text{He}$.

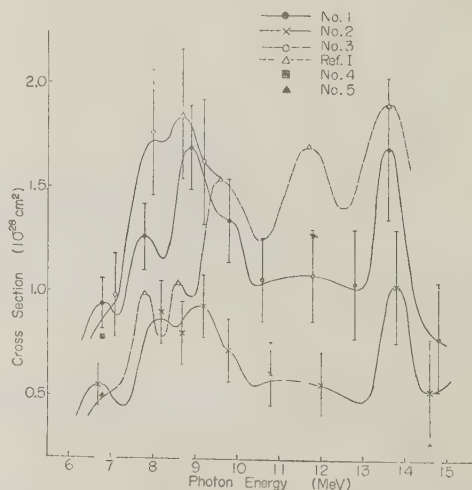


Fig. 2. Excitation function of the reaction ${}^7\text{Li}(\gamma)t{}^4\text{He}$.

poor accuracy in dose determination in the present experiment, and are shown only for demonstrating the mutual consistency of the separate measurements. Apparent resonance peaks obtained from the statistically more reliable data are tabulated in Table II, together with those found in I and the known levels of ${}^7\text{Li}$ compiled by Ajzenberg-Selove and Lauritsen⁴.

Table II.

Plate	Resonance Peaks (MeV)				
No. 1	6.8	7.8	8.9 (9.8)	13.5	
2	6.7	(7.8)	9.0	(13.8)	
3	(7.0)	(8.0)	8.8		
Ref. I	7.6	8.6	9.6	11.7	(13.5)
Ajzenberg and Lauritsen	6.54	7.47	9.6	10.8	12.4 14.0

Because of poor statistics, the energy values of corresponding peaks are not in good agreement in some cases and some peaks are even indiscernible in some plates. Angular distributions of the emitted particles therefore has been studied to make sure the existence of resonance peaks observed in the excitation function. If the observed peaks correspond to the resonance absorption of photons by isolated levels of lithium nucleus, the angular distribution of emitted particles in the center of mass system is expected to be symmetric about 90° as will be discussed later, while the distribution for the inter-resonance region exhibit quite a different feature due, in some cases, to interference between adjacent two states of opposite parity.

The angular distributions of tritons in the energy interval of 0.5 MeV at resonance and inter-resonance energies, observed in the plate No. 1, are given in Fig. 3(a). Similar angular distributions at the resonance peaks obtained from the plates Nos. 2, 3 and 4 are also shown in Figs. 3(b), (c) and (d) respectively. As is seen from the figures, all the distributions at resonance peaks except those at 6.8 MeV seem to have the expected symmetry. The distribution at 6.8 MeV, however, suggests asymmetry around 90° in spite of the resonance-like peaks in the excitation functions.

The angular distributions at about 8.9 MeV α -ray energy can be fitted by a function of

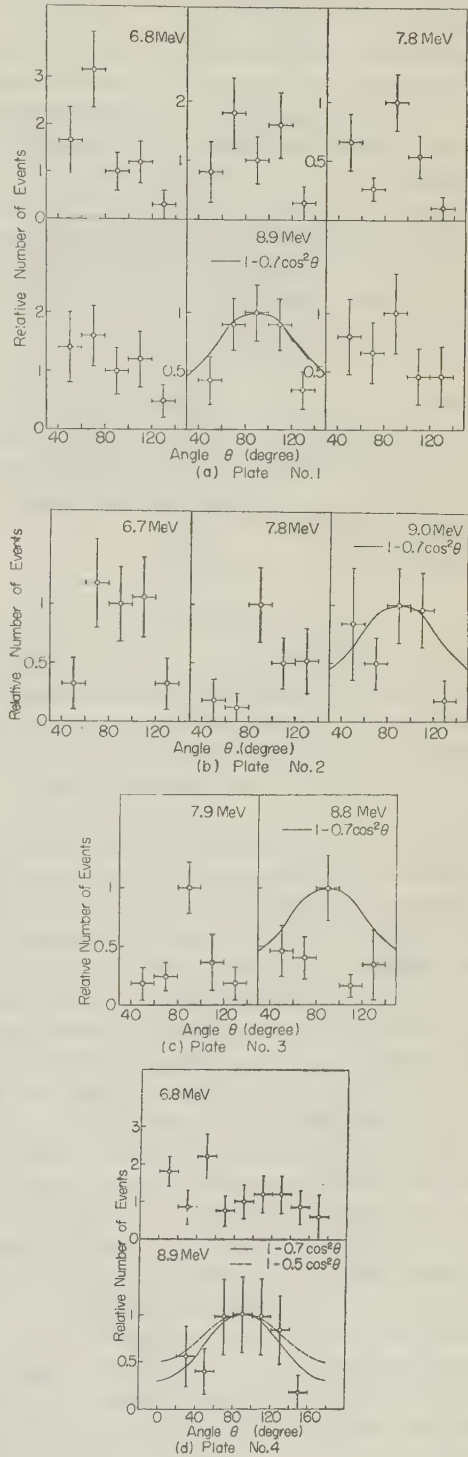


Fig. 3. Angular distribution in the center of mass system of tritons emitted by the reaction ${}^7\text{Li}({}_T){}^4\text{He}$. Ordinates are in arbitrary units.

the form $a - b \cos^2 \theta$, a/b being 0.7. As to the peak around 7.8 Mev, definite conclusion on the angular distribution was hardly possible because of the lack of information in sufficiently wide range of angle. Nevertheless, most likely distribution function seems to be $a - b \cos^2 \theta$, in which a/b varies from 0.6 to 1.0 depending on the interpretation of the data.

These angular distributions can be compared with those derived theoretically by Morita et al.⁵⁾ They have given a general expression for the differential cross section for photo-reaction of the type

$$\gamma + X = Y + b.$$

If we assume that only one separate level of ${}^7\text{Li}$ nucleus takes part in the reaction, and that photons of definite type and multipolarity are absorbed by the nucleus, Morita's formula reduces to the form

$$f(\theta) = \sum_k (LL1 - 1 | LLk0) \cdot W(LJLJ; 3/2k) \cdot Z(I'J'J; 1/2k) \cdot P_k(\cos \theta) \quad (1)^*$$

with the restriction $2L - k = \text{even}$, where L and J represent respectively the total angular momentum of the photon and the compound nucleus, and I' is the orbital angular momentum of the alpha-triton system in the final state.

The angular distribution for the resonance at 8.9 Mev can be reasonably interpreted, if we assume the level to have the spin of 5/2 and to absorb electric dipole or magnetic dipole radiation. In either case, the formula (1) gives an angular distribution of the form $1 - 0.5 \cos^2 \theta$, which is in fair agreement with that obtained in the present experiment. Therefore, 5/2 is most likely assigned for the spin of the level at 8.9 Mev. Other spin values than 5/2 and the absorption of higher multipole radiation as well may be ruled out from the angular distribution consideration.

For the resonance peak at 7.8 Mev, although the same transition seems to be most probable in view of the angular distribution, another possibility of the transition in which a level with spin 5/2 absorbs electric quadrupole radiation may not be excluded. In this case the angular distribution is represented

by $1 - 1.8 \cos^2 \theta + 2.5 \cos^4 \theta$. In any case, most favorable value for the spin of 7.8 Mev level is 5/2. Other possibility will be again excluded by comparing the experimental distribution with those calculated from the formula (1).

An asymmetric angular distribution may be interpreted in terms of interference between two states of opposite parity. The interference effect contributing to the angular distribution for the inter-resonance regions will be qualitatively argued, by making use of the formula derived by Morita et al. (Eq. (15) of ref. 5).

If we assume that the level at 7.8 Mev corresponds to the known level of odd parity with $J=5/2$ and that the level at 8.9 Mev has $5/2^+$, angular distributions calculated for the region between these levels give the form $a + b \cos \theta - c \cos^2 \theta$. This is just the case for the angular distribution shown in Fig. 3(a). If the level at 8.9 Mev has odd parity, the distribution will be symmetric around 90° . Hence we conclude that the level at about 8.9 Mev has $J=5/2$ and even parity.

Asymmetry in the angular distribution for the resonance like region around 6.8 Mev hardly be explained by the interference effect due to the known levels of $3/2^+$ at 6.5 Mev and that of $5/2^-$ at 7.5 Mev. (one more level may be assumed to exist between these two levels, which will cause the angular distribution for the 6.8 Mev region to have the form of $a + b \cos \theta + c \cos^2 \theta$. Detailed discussion, however, will be worth little because of the poor statistics of the present data.)

The resonance at 9.6 Mev found in I is not separated well in this experiment. However, a hump on the excitation curve favours the existence of a resonance peak. Rybka and Katz⁷⁾ have reported a level at 9.66 Mev found in the (γn) process of lithium nucleus.

Although we have not investigated angular distributions for the peak at about 13.5 Mev, existence of a level is quite probable. Romanowaki and Voelker⁸⁾ has studied the photoneutron cross section of ${}^7\text{Li}$ and found a broad resonance peak around 14 Mev. Heinrich and Rubin⁹⁾ have also found a peak centered around 15 Mev in the cross section curve of the reaction ${}^7\text{Li}(\gamma n){}^6\text{Li}$. The peak at about 13.5 Mev found in the present work perhaps corresponds to the resonances re-

* Erdős et al.⁶⁾ has previously calculated the angular distribution function for the reaction ${}^7\text{Li}(\gamma t){}^4\text{He}$ which is identical with (1).

ported in these (γn) experiments. But Rybka and Katz obtained a quite different excitation curve for the same reaction.

In the preceding arguments, we have not considered the effect of "two body" mechanism on the angular distribution of the reaction products. Czyż¹⁰⁾ has investigated the cross section of the reaction ${}^7\text{Li}(\gamma t){}^4\text{He}$ on the basis of two body mechanism, and explained the gross structure of the excitation function. But, as is guessed from Fig. 3, this process will contribute to the cross section as a rather smooth background superposing on sharp resonance peaks and may not be so large as to alter the form of angular distribution.

In conclusion the authors wish to express their gratitude to Mr. K. Kuriyama and Mr. T. Akiba for their collaboration in exposing the plates and to Mr. F. Shiga for his assistance in the scanning work. This work was

partly supported by a grant-in-aid for scientific research of the Ministry of Education.

References

- 1) M. Miwa: J. Phys. Soc. Japan **10** (1955) 173.
- 2) J. Rotblat: Nature **165** (1950) 387.
- 3) M. Wächter: Diplomarbeit, E. T. H. (1954).
- 4) F. Ajzenberg-Selove and T. Lauritsen: Nucl. Phys. **11** (1959) 1.
- 5) M. Morita, A. Sugie and S. Yoshida: Progr. Theor. Phys. **12** (1954) 713.
- 6) P. Erdős, P. Stoll and M. Wächter: Nuovo Cimento **12** (1954) 639.
- 7) T. W. Rybka and L. Katz: Phys. Rev. **110** (1958) 1123.
- 8) T. A. Romanowski and V. H. Voelker: Phys. Rev. **113** (1959) 886.
- 9) F. Heinrich and R. Rubin: Helv. Phys. Acta. **28** (1955) 186.
- 10) W. Czyż: Acta Phys. Polonica **15** (1956) 129.

Reactions of Argon-40 with Alpha-Particles

By Shigeo TANAKA,* Michiaki FURUKAWA,* Takashi MIKUMO,*
Shiro IWATA,** Masuo YAGI*** and Hiroshi AMANO****

*Institute for Nuclear Study, University of Tokyo,
Tanashi-machi, Tokyo*

(Received February 5, 1960)

Excitation functions for the (α, p) and (α, pn) reactions on A^{40} were measured by the activation method using a "modified stacked-foil" technique. The bombardments were made with an alpha-particle beam from the 160 cm INSJ cyclotron. The beam was collected in a Faraday cup and measured by a current integrator. The disintegration rates of product nuclei were determined by $4\pi\beta$ -counting. The results were compared with the predictions based on the statistical model of nuclear reaction by use of a level density expression of the form $\omega = c \exp[2(aE)^{1/2}]$. The experimental cross sections appear to agree with the calculated values for $r_0 \approx 1.1 \times 10^{-13}$ cm and $a = 1 \sim 2$ Mev $^{-1}$. The considerably low value of r_0 might indicate that the statistical model is not completely applicable.

§ 1. Introduction

It has been reported¹⁻²⁾ that the bombardment of argon with alpha-particles results in the production of K^{43} and K^{42} in high yields. Neither the absolute cross section nor the excitation curve of the (α, p) and the (α, pn) reaction of A^{40} has been measured. It is of interest to elucidate whether the cross sections of these reactions are really exceptionally large, as compared with the predictions based on the statistical theory of nuclear reaction. As few data³⁻⁶⁾ are available on the cross sections of alpha-induced reactions, accumulation of more experimental data is desirable for further developments on the elucidation of nuclear reaction mechanism. This experiment is a part of the present authors' study⁷⁾ in which the cross sections of alpha-induced reactions on medium weight nuclei at intermediate energies of alpha-particles are studied.

In this experiment, excitation functions for the (α, p) and the (α, pn) reaction on A^{40} were measured for alpha-particle energies up to 36 Mev. Argon gas was bombarded with

an alpha-particle beam from the 160 cm INSJ cyclotron. In order to measure the energy dependence of cross sections, a "stacked-gas" technique was developed. The disintegration rates of the product nuclei (K^{43} and K^{42}) were measured by $4\pi\beta$ -counting and the energy dependence of the yields was obtained by gamma-ray countings with an NaI(Tl) scintillation spectrometer.

§ 2. Experimental

Bombardments

The deflected beam from the 160 cm INSJ cyclotron was focused by a pair of quadrupole magnets and by a sector-type focusing magnet and led through a concrete wall to the Measuring Room. In different experiments, the energies of the deflected beam were 40.0 Mev and 32.0 Mev as calculated from the cyclotron frequencies. The energy spread of the incident beam was estimated to be less than $\pm 1\%$. The change in frequency during the bombardment was monitored and was less than $\pm 0.5\%$. At the end of the beam duct was placed a rectangular gas chamber which also served as a Faraday cup. (Fig. 1.) In front of this cup there were narrow carbon slits. (not shown in Fig. 1.) The gas chamber was filled with pure argon gas (760 mm Hg) which was separated from the vacuum beam duct by an aluminum foil of 50μ thickness.

To determine the energy dependence of

* Institute for Nuclear study, University of Tokyo, Tokyo.

** Faculty of Science, Osaka University, Osaka.

*** Radiochemical Laboratory, Shizuoka University, Shizuoka.

**** The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai.

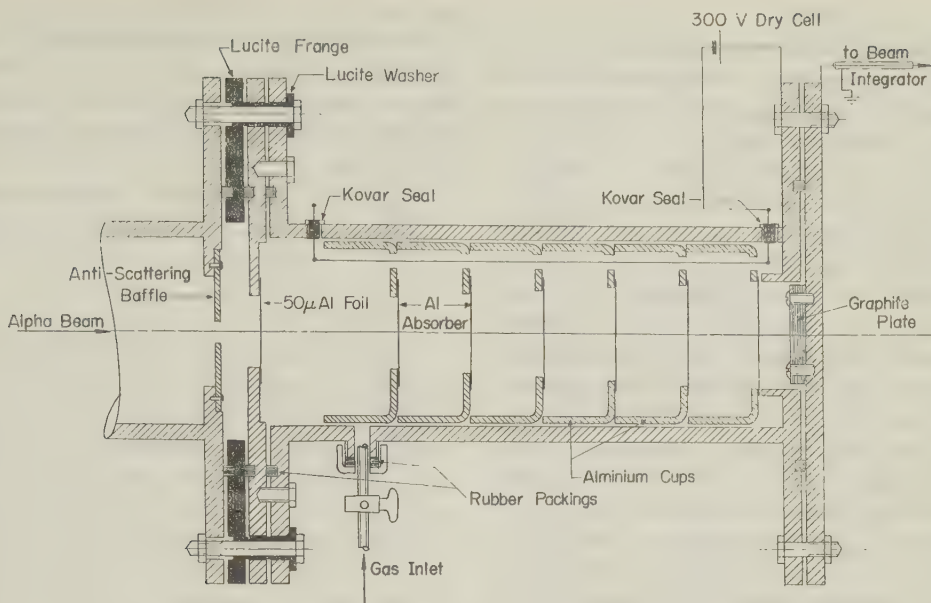


Fig. 1. Illustration of gas chamber (Faraday cup).

cross sections, a "stacked-gas" technique was used. In the gas chamber the argon gas was divided by six aluminum square cups, with holes in their bases forming diaphragms. Aluminum absorbers of appropriate thicknesses were placed on the centre holes of the diaphragms so as to let the beam pass through and degrade its energy. The energies of alpha-particles just entering and leaving each target gas were determined by calculating the energy loss in each section of argon gas in the stack. The energy loss of alpha-particles in each aluminum absorber and in each section of argon gas were calculated from the range-energy curves of Aron et al.⁸⁾ Each diaphragm had a small hole at one corner through which was stretched a platinum wire supplied with a potential of -300 V with respect to the Faraday cup by a dry-cell, isolated from the ground. It was expected that almost all the potassium ions produced by $A^{40}(\alpha, p)$ and $A^{40}(\alpha, pn)$ reaction could be collected on this platinum wire without losing all of the charge through collisions with argon atoms. The centre holes in the bottom of the aluminum diaphragms were so large that the alpha-particle beam reached the graphite plate at the end of the Faraday cup. Total charge of the beam was measured by a 100% feedback type beam current integrator.

Chemical procedures

After the bombardment, the argon gas was pumped out and passed through a washing bottle filled with dilute hydrochloric acid in order to absorb radioactive potassium remaining in the gas. The washing solution was evaporated to 2 ml. The platinum wire was thereafter removed and cut into six pieces, each piece corresponding to each gas section. The activities on each piece were leached with 2 ml. of dilute hydrochloric acid and measured with a constant geometry. Radioactive products remaining in the sections were removed with 2~5 ml. of dilute potassium hydroxide solution. The washing solutions were neutralized with hydrochloric acid and evaporated to 2 ml. All the samples were adjusted to a constant volume of 2 ml. and were put in polyethylene vessels.

Relative gamma-counting

These samples were submitted to a scintillation spectrometer with a 2 in. dia. $\times$ 2 in. thick NaI (Tl) crystal and a Dumont type 6292 photo-multiplier. The relative yields of K^{43} were obtained from photo-peaks at 0.37 Mev and 0.61 Mev after subtraction of Compton tails from the 1.53 Mev gamma-ray emitted from K^{42} . Relative yields of K^{42} were given by counting with the spectrometer biased to eliminate gamma-rays below 1 Mev. This discriminates K^{42} against K^{43} .

Absolute beta-counting

The disintegration rate was determined by $4\pi\beta$ -counting method. With this technique, absolute beta-counting for a β^- -emitter can be done within an accuracy of about 2%, provided the counting system is properly adjusted. In this work Q-gas was used as the counting gas. The counter was operated in the Geiger region (about 1.25 kV), but the counting rate was kept moderate. In most cases, the total background of the counter was about 100 counts per minute. The source was mounted on a thin gold-sputtered polyvinyl acetate film whose thickness was about $50 \mu\text{g}/\text{cm}^2$. A small absorption correction was made. A self-absorption correction was not made, but should be very small in this experiment. The disintegration rate of K^{43} was determined by applying the above procedures to a sample below the threshold of the $\text{A}^{40}(\alpha, pn)\text{K}^{42}$ reaction. The disintegration rate of K^{42} was determined, after the contribution from K^{43} activity was subtracted by analysing the decay curve from Geiger counting.

When the sample solution of almost carrier-free potassium was dispensed using glass pipettes and beakers, the activity loss by adsorption on the wall of glass vessel was of question. This loss was estimated not to exceed 10% of the total activity.

§ 3. Results

With the present technique, a most part of the activity was found on the platinum wire. The activity remaining in the argon gas and on the wall of the aluminum cups and of the Faraday cup was examined, and was less than 20% of the total activity. This activity was involved in the calculation of the cross sections. As the effect of the field distortions near the end of the wire was not corrected, the result from the end diaphragm was ignored. The fraction of the activity which migrate from one section to another was estimated to be very small.

The cross sections were calculated in a direct manner using the values of half-life; 22.4 h for K^{43} and 12.4 h for K^{42} . These were obtained from the compilation of Strominger et al.⁹⁾ The cross sections are plotted as a function of alpha-particle energy in Fig. 2, together with the energy with in the target

gas and with the estimated standard error of the magnitude of cross section. The excitation function for the (α, p) reaction attains its maximum value at about 18 Mev and decreases rather slowly at higher energies.

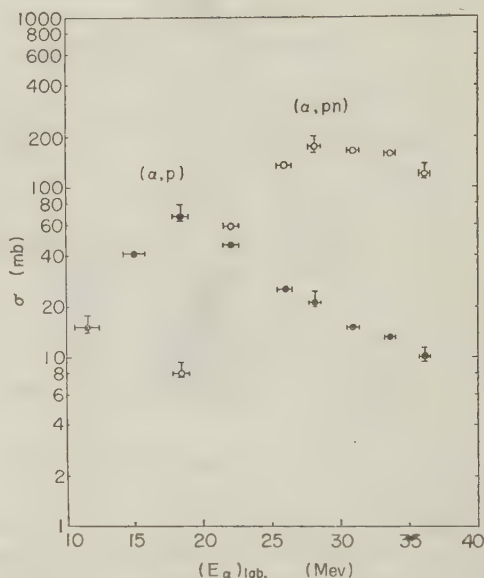


Fig. 2. Excitation functions for the (α, p) and the (α, pn) reaction on A^{40} .

§ 4. Discussion

The angular distributions of protons emitted by the (α, p) reactions leaving the residual nuclei in low-lying states have, in general, forward peaks for many of the medium weight nuclei, including A^{40} , at intermediate energies.¹⁰⁾ Most of the alpha-induced reactions leaving the residual nuclei in low-lying states seem to proceed by direct interaction. In contrast, the cross sections of alpha-induced reactions obtained by the activation method, e.g. on Mn^{55} , Cu^{63} , Cu^{65} and Ag^{109} , agree fairly well with the calculations based on the statistical model of nuclear reaction, so the compound nucleus formation process may be of predominant importance.^{4), 7), 11)}

From this point of view, a comparison of the observed cross sections with those predicted by the statistical model of nuclear reaction is of some interest, although it might be expected that A^{40} is too light in weight to be treated on a statistical foundation.

It was assumed that neutrons, protons and alpha-particles were the only particles involved. The evaporation of deuterons would

increase the (α, pn) reaction cross section, but this type of process appears to be negligible because of their small probability of existence at the nuclear surface and of the difficulty in penetrating the Coulomb barrier.¹²⁾ Tritons would be in the same situation as deuterons. The cross sections for (α, p) and (α, pn) reaction may be written¹³⁾

$$\sigma(\alpha, p) = \sigma_c(E_\alpha) \cdot f_p / \sum_i f_i$$

and

$$\sigma(\alpha, pn) = \sigma_c(E_\alpha) \cdot (f_{pn} + f_{np}) / \sum_i f_i.$$

Where $\sigma_c(E_\alpha)$ is the cross section for the formation of compound nucleus at an incident energy of alpha-particles E_α . The quantities f_p , f_{pn} and f_{np} are proportional to the probabilities for the emission of a proton alone, of a proton followed by a neutron and of a neutron followed by a proton, respectively. $\sum_i f_i$ is a quantity proportional to the sum of the emission probabilities of all the probable modes of decay. The values of $\sigma_c(E_\alpha)$ as well as the cross sections for the inverse process were taken from Shapiro's calculation.¹⁴⁾ The inverse reaction cross section for neutrons was taken as the geometric cross section πR^2 of the product nucleus. It was assumed that the interaction radius R was expressed by $R = r_0 \times A^{1/3} + \rho_i$. ρ_i was taken as 1.21×10^{-13} cm for alpha-particles, and zero for protons and neutrons. The values of nuclear binding energy were obtained from the compilation of Wapstra.¹⁵⁾ The level density ω of residual nucleus was assumed to be given by the expression $\omega = c \exp [2(aE)^{1/2}]$, in which a and c were constants. The dependence of level density on odd-odd, odd-even, even-odd and even-even nucleus was taken into account as follows.¹⁷⁾

$$\frac{\omega_{0-0}}{12} \sim \frac{\omega_{0-e}}{5} \sim \frac{\omega_{e-e}}{1}, \quad \omega_{0-e} - \omega_{e-0},$$

The values of r_0 and a used in the calculation were left as adjustable parameters to be determined by comparison with the experimental results.

The comparison of experimental and calculated values is given in Figs. 3~5.

Fig. 3 shows the dependence of the excitation functions on the value of a with $r_0 = 1.3 \times 10^{-13}$ cm. This comparison appears to show that $a = 1 \text{ Mev}^{-1}$ is favourable to fit the experimental data of the energy dependence for the (α, p) reaction, and $a = 2 \text{ Mev}^{-1}$ for the

(α, pn) reaction. The experimental cross sections agree fairly well with the calculated values for $r_0 = 1.1 \times 10^{-13}$ cm and $a = 1 \text{ Mev}^{-1}$. (Fig. 4) The con-

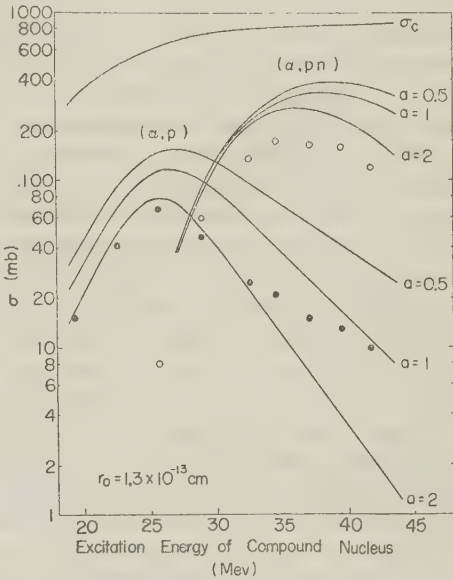


Fig. 3. Comparison of the experimental and calculated excitation functions. Calculated curves on the basis $r_0 = 1.3 \times 10^{-13}$ cm for different values of a are shown.

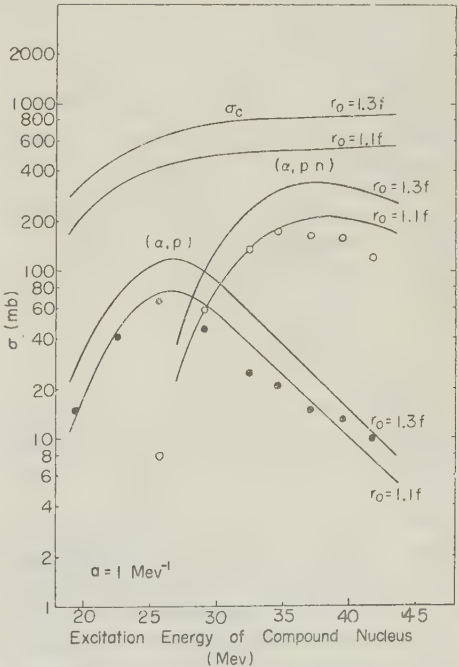


Fig. 4. Comparison of the experimental and calculated excitation functions. Calculated curves on the basis $a = 1 \text{ Mev}^{-1}$ for different values of r_0 are shown. $f = 1 \times 10^{-13}$ cm.

siderably low value of r_0 required to fit the experimental data is inconsistent with the previous experiments. In the alpha-induced reactions measured to date, for many of the medium weight nuclei, $48 \leq A \leq 110$, the cross section for the formation of compound nucleus is consistent with $r_0 = (1.6 \pm 0.1) \times 10^{-13}$ cm.^{4), 6), 7), 11)} Most of the excitation functions measured to date appear to be consistent with $a \approx 2$ Mev⁻¹, regardless of mass number. According to the Fermi gas model, however, a is proportional to the mass number of the residual nucleus in question, and this prediction has been exhibited indeed from several measurements of energy spectra of emitted particles.¹⁶⁾ In this situation, the smaller value of a ($a = 1$ Mev⁻¹) for this mass region might be not necessarily inconsistent with the previously obtained value of a ($a = 2$ Mev⁻¹) for the medium weight nuclei.

Another agreement between experimental and calculated values seems to be obtained for $a = 2$ Mev⁻¹ and $r_0 = (1.1 \sim 1.2) \times 10^{-13}$ cm. (Fig. 5) In this case, the experimental cross sections for the (α, p) reaction above the threshold energy for a secondary particle emission exceed the calculated values. This

discrepancy might suggest a contribution of some reaction mechanism without passing through the compound nucleus formation process.

In view of the assumptions in the calculation, especially the rough consideration for the level density of the individual residual nucleus, the above results may not be taken as evidence for or against compound nucleus mechanism. Furthermore, it is in doubt whether the statistical model applies exactly to a nucleus as light as A^{40} . However, in view of the above inconsistencies, it seems desirable to make further excitation-function measurements in the light-element region in order to obtain a more decisive conclusion on the reaction mechanism.

Authors' thanks are due to Prof. I. Nonaka and the other members of staff of Low Energy Division in this Institute for their interest and encouragement. They are also grateful to the Cyclotron Crew for their cyclotron operation.

References

- 1) R. Overstreet and L. Jacobson: Phys. Rev. **72** (1947) 349.
- 2) R. Overstreet, L. Jacobson and P. R. Stout: Phys. Rev. **75** (1949) 231.
- 3) S. N. Ghoshal: Phys. Rev. **80** (1950) 939.
- 4) E. Bleuler, A. K. Stebbins and D. J. Tendam: Phys. Rev. **90** (1953) 460.
- 5) K. G. Porges: Phys. Rev. **101** (1956) 225.
- 6) N. T. Porile: Phys. Rev. **115** (1959) 939.
- 7) S. Tanaka et al.: J. Phys. Soc. Japan **15** (1960) 545.
- 8) W. A. Aron, B. G. Hoffman and F. C. Williams: U. S. Atomic Energy Commission Report. AECU-663 (1949).
- 9) D. Strominger, J. M. Hollander and G. T. Seaborg: Rev. Mod. Phys. **30** (1958) 585.
- 10) I. Nonaka et al.: to be published in J. Phys. Soc. Japan.
- 11) N. T. Porile and D. L. Morrison: Phys. Rev. **116** (1959) 1193.
- 12) K. Kikuchi: Progr. Theor. Phys. **18** (1957) 503.
- 13) J. B. Blatt and V. F. Weisskopf: *Theoretical Nuclear Physics* (John Wiley, New York, 1953).
- 14) M. M. Shapiro: Phys. Rev. **90** (1953) 171.
- 15) A. H. Wapstra: *Handbuch der Physik* Vol. **38-1** (Springer Verlag, 1958).
- 16) G. Igo and H. E. Wegner: Phys. Rev. **102** (1956) 1365.
- 17) G. Brown and H. Muirhead: Phil. Mag. **2** (1957) 473.

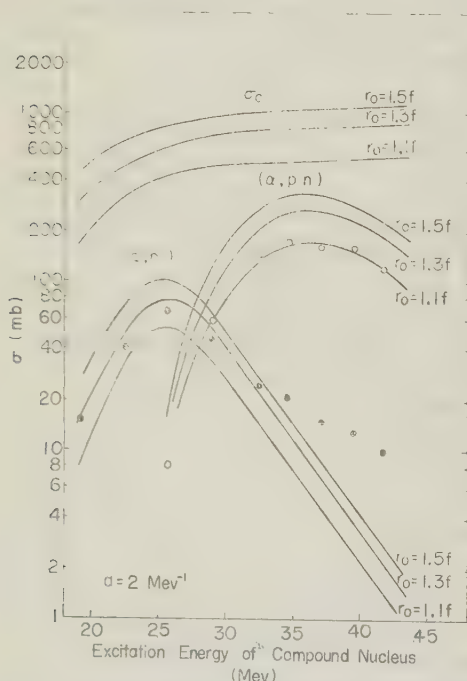


Fig. 5. Comparison of the experimental and calculated excitation functions. Calculated curves on the basis $a = 2$ MeV⁻¹ for different values of r_0 are shown. $f = 1 \times 10^{-13}$ cm.

On the First and the Second Excited States in Ge^{74}

By Toshimitsu YAMAZAKI, Hidetsugu Ikegami and Mitsuo SAKAI

*Institute for Nuclear Study, University of Tokyo, Tanashi-machi,
Kitatama-gun, Tokyo, Japan*

(Received February 6, 1960)

The first and the second excited states in Ge^{74} were studied in detail from the decay of As^{74} . The possibility of the presence of 0^+ excited level was checked by searching for an internal conversion line corresponding to $E0$ transition by means of a beta-ray spectrometer, but no detectable peak was observed. From the gamma-gamma coincidence measurements the relative intensity $T(2' \rightarrow 2)/T(2' \rightarrow 0)$ was obtained to be 1.7. From the gamma-gamma angular-correlation measurements the spin of the second excited state was assigned to be 2 and the $E2/M1$ mixing ratio δ in the $2' \rightarrow 2$ gamma transition was found to be $-\begin{pmatrix} 1 & -1.9 \\ & -0.5 \end{pmatrix}$. These results were discussed in view of systematics on the medium-weight even-even nuclei.

§ 1. Introduction

Recently many systematic features on medium-weight even-even nuclei were made clear. For these nuclei vibrational models, such as the Scharff-Goldhaber and Weneser's spherical vibrational model¹⁾ and the Wilets and Jean's non-spherical vibrational model²⁾, give fairly successful explanation but are not at all satisfactory, in contrast to the complete success of the Bohr and Mottelson's rotational model³⁾ for heavy nuclei. On the other hand, from a different standpoint, Davydov and Fillipov proposed an axially asymmetric rotor model⁴⁾, which describes excited states of medium-weight nuclei as well as heavy nuclei by two deformation parameters. With such developments in nuclear models, it becomes very important to make clear systematic properties of excited states, such as not only level spacings and spin sequences, but also absolute and relative transition probabilities (level-lives and branching ratios), multipole mixing ratios and its phases of gamma transitions and $f\tau$ -values in beta decays.

From such a view point, the excited states of Ge^{74} , which belongs to so called⁵⁾ 1st $S(2)$ group ($38 \leq N \leq 48$), were studied from the decay of 17.5-day As^{74} . Previously, from the beta-ray spectrometer measurements of As^{74} by Johansson et al.⁶⁾, only the first 596 KeV level in Ge^{74} and the first 635 KeV level in Se^{74} were known. Recently the presence of the second 1200 KeV level, which was suggested by Sinclair⁷⁾ from the experiment on

neutron inelastic scattering, was verified. Grigoriev et al.⁸⁾ found a weak 1200 KeV gamma ray from the external conversion electron spectrum of As^{74} . Horen et al.^{9), 10)} found, by scintillation spectrometry, not only the second level but also the third 2.2 MeV level and proposed a new decay scheme, as given in Fig. 1. McGowan and Stelson¹¹⁾ reported that the second 1200 KeV level in Ge^{74} was observed by the Coulomb excitation.*

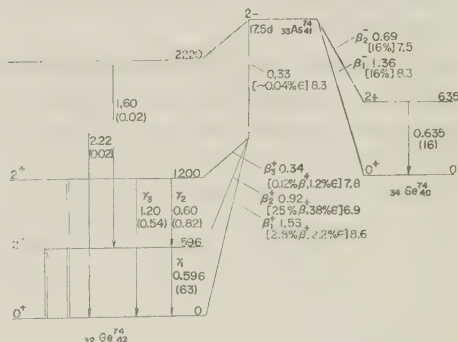


Fig. 1. Decay scheme for As^{74} as proposed by Horen et al. Some values are modified by the present authors.

Since the branching ratios of the decay to the second and the higher excited states are very small, precise measurements seemed to be difficult. The present work was focused to search for low lying 0^+ level, to measure the relative transition probability of the cas-

* Note added in proof.— After having written this article, the authors noticed other works^{26), 27)} on the excited states in Ge^{74} .

cade gamma ray to the crossover gamma ray from the second excited state and to determine the E2/M1 mixing ratio of the cascade gamma ray.

§ 2. Source Preparation

The As^{74} activity was produced by Ge^{74} (p, n) As^{74} reaction. Natural GeO_2 powder was bombarded with the 14 MeV proton beam of about 20 μA for 6 hours in the INS 160 cm cyclotron. After the bombardment, the arsenic activities were chemically separated. The arsenic samples for gamma-ray measurements were obtained in As_2S_5 form with carrier. For beta-ray measurements an almost carrier-free sample was prepared in arsenate form, which was carefully mounted on a 200 $\mu\text{g}/\text{cm}^2$ thick vinyl chloride membrane. The chemical procedure will be described in detail elsewhere by K. Saito et al.¹²⁾ The measurements on As^{74} were started more than ten days after the bombardment, when other shorter lived activities, such as As^{70} , As^{72} and As^{76} , vanished completely. The 76-day activity of As^{78} affected no disturbance, since it decays solely by electron capture and has only two very soft gamma rays¹³⁾.

§ 3. The Search for a 0^+ Excited State in Ge^{74} and Se^{74}

From the systematics of low-lying excited levels in the germanium isotopes presented in Fig. 2, one can expect the presence of a low-lying 0^+ excited state in Ge^{74} and Se^{74} . If this were the case, the decay populated to

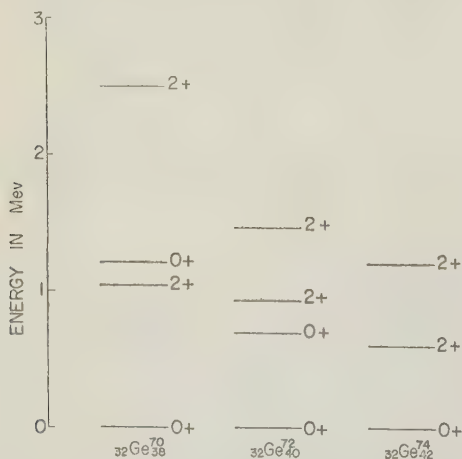


Fig. 2. Low-lying excited states of germanium isotopes.

this level should be deexcited to the ground state by emitting uniquely the internally conversion electrons by a beta-ray spectrometer was considered as the best method for the detection of this level.

As almost carrier-free source, 3-mm wide and 25 mm long, was put in the INS III beta-ray spectrometer*. The resolution was found to be 0.8%. The electron spectrum in the region between 200 and 720 KeV was shown in Fig. 3. Any electron peak could not be observed except the K- and L+M-conversion lines of the 596 KeV gamma ray in Ge^{74} and the 635 KeV gamma ray in Se^{74} , which were already reported by Grigoriev et al⁸⁾.

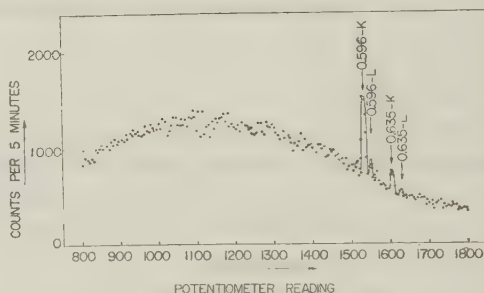


Fig. 3. Beta spectrum of As^{74} in the region between 200 and 720 KeV.

From the statistic consideration of the measurement it was concluded that the peak of one sixth of the intensity of the 596 KeV K-line can be detected. In taking account of the K-conversion coefficient 1.2×10^{-3} for this gamma ray obtained by the interpolation of the values in the Rose's table¹⁵⁾ and in taking account of the branching ratio 62%⁸⁾ of the decay involved in this excited level, the upper limit of the branching ratio of the decay via the 0^+ level was found to be 3.3×10^{-4} . Assuming that this 0^+ level is at 500 KeV, the $\log f\tau$ value of the beta transition to this level can be deduced by using the Moszkowski diagram¹⁶⁾ and by adopting the upper limit of the branching ratio. One can find it is more than 10.0. Of course, one can not exclude that possibility of the presence of 0^+ level from the present measurement. A further precise measurement would be expected.

* The INS III beta-ray spectrometer is a sector-type double-focusing magnetic spectrometer of radius=18 cm¹⁴⁾.

§ 4. The Single and Coincidence Spectra of the Gamma Rays in Ge^{74} .

The gamma-ray spectra were measured using a $1\frac{1}{2}''\phi\times 2''$ NaI (TI) crystal coupled with an RCA-6342 photomultiplier and an INS 20-Channel Pulse Height Analyser. The source, covered with a Lucite beta absorber of enough thickness, was placed at various distances from the detector. Since the intensities of the gamma rays are very much weak above 635 KeV, the solid-angle addition of the two intense coincident gamma rays of 510 and 596 KeV have much contribution to the pulse height spectra above 700 KeV, as shown in Fig. 4. By changing the solid angle it is

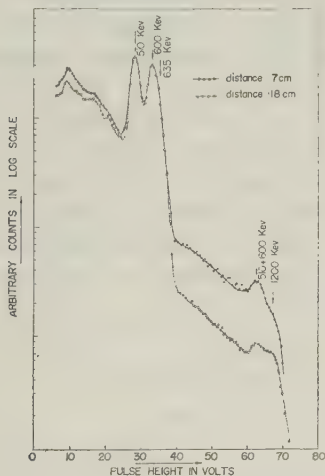


Fig. 4. Single scintillation spectra of the gamma rays from As^{74} .

Table I. Relative intensities of gamma rays in Ge^{74} .

Gamma-ray energy in KeV		Relative intensity		
		Present	Horen et al.	Grigoriev et al.
γ_1	596	100	100	100
γ_2	600	1.3 ± 0.3	0.21	—
γ_3	1200	0.77 ± 0.10	0.86 ± 0.09	0.43
$2\gamma^\pm$	510	90	92 ± 9	—

verified that the peak at 1200 KeV is a true photo-peak, but that the peak at 1100 KeV was merely a sum peak. No other distinct peak was found under 1200 KeV. The continuous tail above 700 KeV was then thought to consist mainly of the 1200 KeV gamma ray, the bremsstrahlung of the beta rays and the annihilation in flight of the positrons⁽⁷⁾. From

these spectra the relative intensities were obtained in Table I, which were in good agreement with those of Horen et al⁽¹⁰⁾.

In order to obtain the relative intensity of the cascade 600 KeV gamma ray from the second to the first excited state, the coincidence spectrum with the 600 KeV gamma ray was measured. The signal from the reference detector was sent to the gate of the 20-Channel Pulse Height Analyser after passing through a fast-slow coincidence circuit with the $2\tau=50\mu s$. Each detector was placed at five centimeters from the source and shielded from each other by the lead absorber.

Since the $2'\rightarrow 2$ cascade gamma ray γ_2 is very weak and has the same energy as the intense $2\rightarrow 0$ gamma ray γ_1 , particular cautions should be paid for deriving the relative intensity of the former gamma ray by the coincidence method.

Since the 600-KeV photo-peak was incompletely resolved from the 510 KeV annihilation peak, the position and the width of the gate window was chosen very carefully, as in Fig. 5, for avoiding the contribution from the 510 KeV peak. This effect was checked by

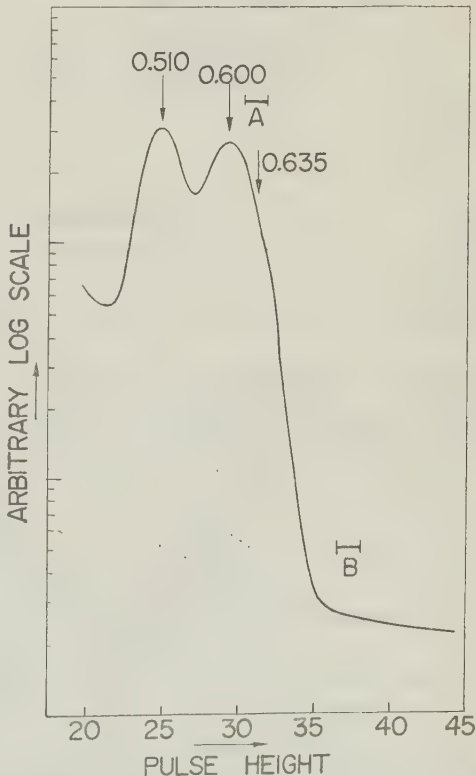


Fig. 5. Gate setting for coincidence measurements.

taking the coincidence spectra for various window settings. So far as the contribution from the upper tail is concerned, it could be easily corrected by subtracting the coincidence spectra with the window set at the upper tail.

In case two gamma rays, one of which has a small branching ratio ξ , are in cascade, the singles and the coincidence counts in a coincidence experiment can be written as $N_1 \approx N\epsilon_1$, $N_2 \approx \xi \cdot N\epsilon_2$ and $N_c = \xi \cdot N\epsilon_1\epsilon_2$, respectively, where ϵ_1 and ϵ_2 are the overall detecting efficiencies for each detector, of which the gate is set at each photo-peak. Hence, we get $N_{co}/N_c \approx 2\tau N$. In the present case, however, where the energies are the same, singles and the coincidence counts become $N_1 \approx (1+\xi)N\epsilon_1$, $N_2 \approx (1+\xi)N\epsilon_2$ and $N_c = \xi \cdot N\epsilon_1\epsilon_2$. Hence, we have $N_{co}/N_c \approx 2\tau N(1+\xi)^2/\xi$ which is about ξ times smaller than that in an ordinary case. Therefore, it is required that the coincidence resolving time is made as short as possible and the source intensity is

kept much weaker than in a usual case. The present measurement was carried out with 2τ of 5×10^{-8} sec and with the source of about one microcurie.

By setting the gate of the reference detector at B in Fig. 5, the coincidence spectra were first measured. As shown in Fig. 6, the two spectra with the angles between two detectors of 90° and 180° are considerably different. First, the 510 KeV peak is extremely higher at $\theta=180^\circ$ than at $\theta=90^\circ$, which is easily explained as the coincidence of the 510 KeV annihilation quanta with the solid-angle addition of the partner quanta and the 600 KeV gamma ray at $\theta=180^\circ$. Secondly, the continuous tail above the 600 KeV peak is higher at $\theta=180^\circ$, while it is nearly zero at $\theta=90^\circ$. This point, being serious in angular correlation measurements, will be discussed later.

On a basis of these preliminary measurements, the coincidence spectrum with the 600 KeV peak (window A in Fig. 5) was measured at $\theta=90^\circ$ and corrected for coincidence with the tail. Fig. 7 shows a final result, from which one can obtain the branching ratio ξ

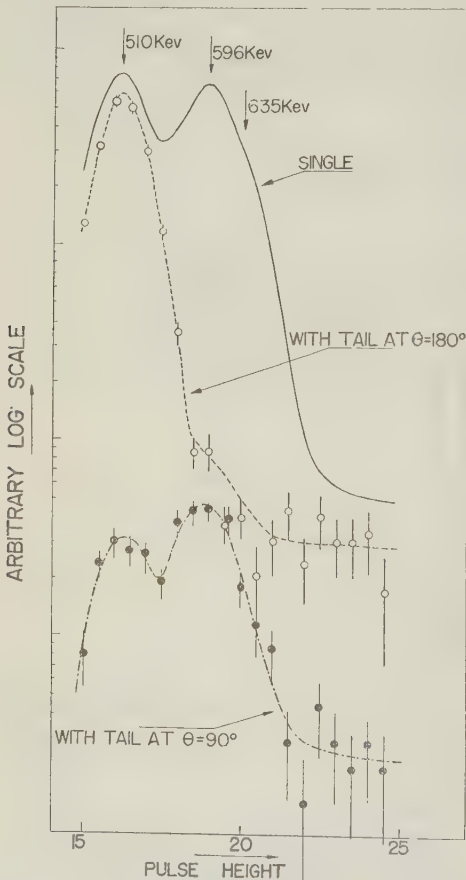


Fig. 6. Coincidence spectra with the upper tail at $\theta=90^\circ$ and $\theta=180^\circ$.

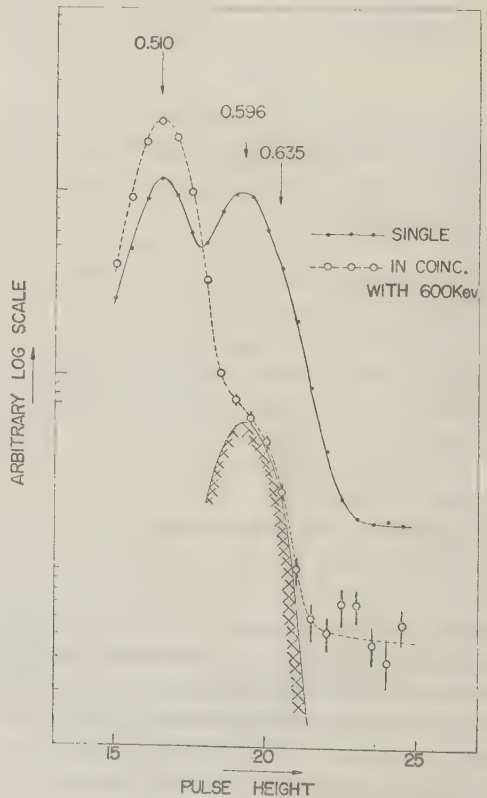


Fig. 7. Corrected coincidence spectrum with the 600 KeV gamma ray.

120° might be due to a kinematical relation between two annihilation in flight radiations (Fig. 10). It seems to be interesting to verify these in detail, but no further experiments were made.

Next, peak—peak angular correlation was measured. In this case windows of both detectors were set at the 600 KeV peak. Coincidence counts were about 27 per an hour. The measurements were continued for 40 days. The pattern thus obtained was corrected for peak—tail and tail—tail coincidences.

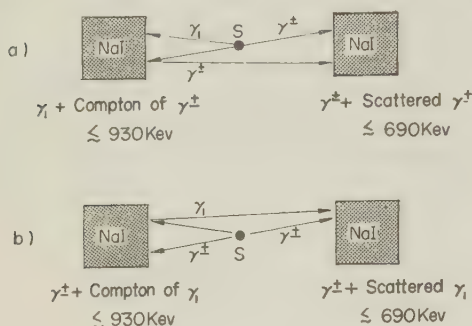


Fig. 9. Scattering effects at $\theta=180^\circ$.

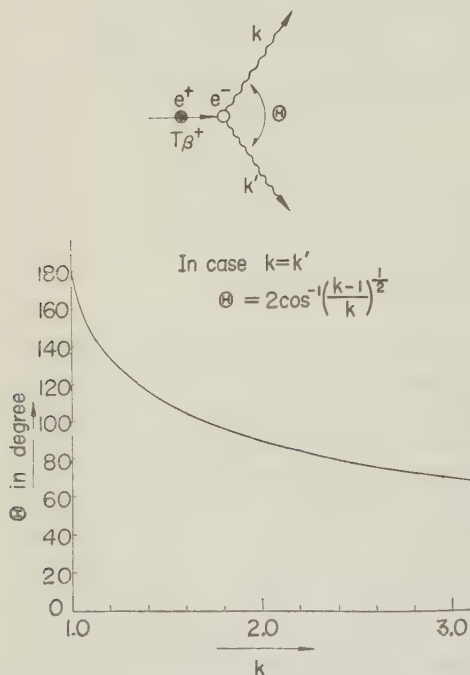


Fig. 10. Kinematic relation between two annihilation in flight gamma rays. In case the energies of the two photons are the same, the angle between them are shown as a simple function of the photon energy (or the incident-positron energy).

The corrected experimental angular-correlation functions for the 600—600 KeV cascade is shown in Fig. 11. The errors were due not only to poor statistics but also to the ambiguities resulting from the corrections. Least-squares fitting gave $A_2' = -0.205 \pm 0.084$ and $A_4' = 0.134 \pm 0.126$. Since the energies are not so different from 510 KeV, the correction for finite solid angle of detectors was made according to the Church and Kraushaar's method¹⁹⁾, using annihilation radiations. The attenuation factors were then found to be $Q_2/Q_0 = 0.89$ and $Q_4/Q_0 = 0.67$. Hence, $A_2 = -0.230 \pm 0.094$ and $A_4 = 0.200 \pm 0.188$.

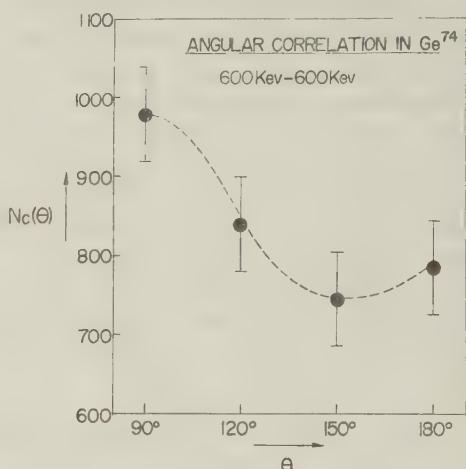


Fig. 11. The corrected angular correlation function of the 600—600 KeV cascade in Ge^{74} .

These values may be fitted to the theoretical ones²⁰⁾ with the spin sequence 2—2—0 with mixing ratio $\delta = -\left(\begin{smallmatrix} 1 & 9 \\ & -0.5 \end{smallmatrix} \right)$. No mixture will fit the spin sequences 3—2—0 and 1—2—0. Hence, it was concluded that the second level has spin of two and the E2/M1 mixing ratio δ of the $2' \rightarrow 2$ transition is $-\left(\begin{smallmatrix} 1 & 9 \\ & -0.5 \end{smallmatrix} \right)$, i.e., $100\% \geq E2 \geq 20\%$.

§ 6. Discussions

A. Level sequence and beta transitions.

A low-lying 0^+ level could not be found by searching for E0 transition. A 0^+ state may exist with rather higher excitation energy.

It was already known from the Coulomb excitation experiment by McGowan and Stelson¹¹⁾ that the second excited state has spin of two. This $0-2-2$ sequence, agreeing with the systematics on medium-weight nuclei,

was now confirmed by the angular-correlation measurement. It can be possible that the 1200 KeV level is a doublet one with 10% mixture of 4+ state, but it would be improbable, since a 4+ level is expected to present at about 1.4 MeV from the systematics of doublets²¹⁾ in medium-weight nuclei. If this expected 4+ state were present, gamma-ray transition to the first 2+ state would occur. No gamma ray of about 800 KeV, however, could be observed. One can then estimate that the lower limit of the $\log f\tau$ value to this 4+ state is about 8.5. Recently one of the authors (M.S.) pointed out²²⁾ from the systematics of beta decays that beta transition from a parent 2- state to a daughter 4+ state is unfavoured. The present case agrees with this systematics. The $\log f\tau$ values of the beta transitions from As⁷⁴ to Ge⁷⁴ are summarized in Table II. It may be worth pointing out that the beta transition to the second 2+ state is unfavoured.

Table II. $\log f\tau$ values of beta transitions from As⁷⁴ to Ge⁷⁴.

Transition	$\log f\tau$ -value
to ground	8.6
to 1st	6.9
to 2nd	7.8

B. Reduced relative transition probability

From the values of the branching ratio and the mixing ratio one can get the reduced relative transition probability:

$$\begin{aligned} \frac{B(E2, 2' \rightarrow 2)}{B(E2, 2' \rightarrow 0)} &= 2^5 \frac{T(E2, 2' \rightarrow 2)}{T(E2, 2' \rightarrow 0)} \\ &= 2^5 \frac{\delta^2}{1 + \delta^2} \cdot \frac{\text{cascade}}{\text{crossover}} = 27 \frac{+27}{-15} \end{aligned}$$

This value is similar to those in many other nuclei. The value obtained by Horen et al. is about one order smaller than the present and differs from systematics.

The systematic trends of these finite values, which can not be followed from pure vibrational models, were explained fairly well by Davydov and Fillipov's asymmetric rotor model^{5), 23)}. For Ge⁷⁴, in which E_2/E_1 is nearly two and γ is about 30°, a very large value is predicted, being inconsistent with the experimental value. But, since this ratio is very sensitive to γ and the E_2/E_1 ratio may be

perturbed by residual interactions, this discrepancy might not have so severe sense.

C. E2/M1 mixing ratio of the 2' → 2 transition.

In order to see the systematics of $E2/M1$ mixing ratio of 2' → 2 transition, the elliptical representation²⁴⁾ of angular-correlation function is presented in Fig. 12 for Ge⁷⁴ and other 1st S(2) nuclei.

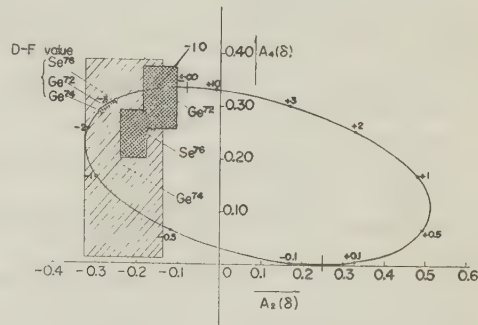


Fig. 12. Elliptical representation of the angular-correlation functions of the 2' → 2 → 0 cascades in Ge⁷⁴, Ge⁷² and Se⁷⁶. The parameter on the ellipse indicates δ . The theoretical values predicted by Davydov and Fillipov are also plotted in the figure.

Recently finite values of mixing ratio, which could not be explained by pure vibrational models, were shown²⁵⁾ to agree fairly well with those predicted by Davydov and Fillipov⁴⁾. For Ge⁷⁴ one obtains $|\delta|=2.7$ from the Davydov-Fillipov formula, being agreeable with the experimental value $\delta = -\begin{pmatrix} +9 \\ 1 - 0.5 \end{pmatrix}$. In

Fig. 12 are plotted also the predicted values.

It was pointed out⁵⁾ from poor statistics that the signs of δ in nuclei with 0-2-2 spin sequence are negative in the regions $38 \leq N \leq 48$ and $110 \leq N \leq 124$ and positive in the region $64 \leq N \leq 74$. The negative sign of δ in Ge⁷⁴ seems to confirm this rule. This rule may be very important for understanding the physical meaning of mixing ratio and the excitation mechanism in these nuclei.

The authors express their thanks to Professor S. Kikuchi and Professor I. Nonaka for their encouragement and interest in the research. The helps given by Dr. K. Saito of the Institute for Nuclear Study and Drs. S. Ikeda and M. Saito of the Research Institute for Iron, Steel and Other Metals, Tohoku University on the chemical separation of radioactive isotope are deeply appreciated.

Their thanks are also due to the cyclotron crew and other members of Low Energy Division of the Institute for Nuclear Study for their kindful cooperations.

References

- 1) G. Scharff-Goldhader and J. Wenenser: Phys. Rev. **98** (1955) 212.
- 2) L. Wilets and M. Jean: Phys. Rev. **102** (1956) 788.
- 3) A. Bohr and B. R. Mottelson: Dan. Mat. Fys. Medd. **27** (1953) No. 16. (1958) 237.
- 5) M. Sakai: Rep. Inst. Nucl. Study, University of Tokyo INSJ-6 Feb. (1958).
- 6) S. Johansson, Y. Cauchois and K. Siegbahn: Phys. Rev. **82** (1951) 275.
- 7) R. M. Sinclair: Phys. Rev. **107** (1957) 1306.
- 8) E. P. Grigoriev, B. S. Dzhelepov, A. V. Zolotavin, V. Ya. Mishin, V. P. Prihodceba, Yu V. Holinov and G. E. Shchkin: Izv. Akad. Nauk S.S.S.R. Ser. Fiz. **22** (1958) 831.
- 9) D. J. Horen and D. O. Wells: Bull. Amer. Phys. Soc. **3** (1958) 315.
- 10) D. J. Horen, W. E. Meyerhof, J. J. Kraushaar, D. O. Wells, E. Brun and J. E. Neighbor: Phys. Rev. **113** (1959) 875.
- 11) F. K. McGowan and P. H. Stelson: Bull. Amer. Phys. Soc. **4** (1959) 232.
- 12) K. Saito, S. Ikeda and M. Saito: Bull. Chem. Soc. Japan. in press.
- 13) K. Way et al.: *Nuclear Level Schemes* (U.S. Atomic Energy Commission).
- 14) M. Sakai and H. Ikegami: J. Phys. Soc. Japan **13** (1958) 1076; M. Sakai, H. Ikegami and T. Yamazaki: to be published.
- 15) M. E. Rose: *Internal Conversion Coefficient* (North Holland Publ. Co., Amsterdam).
- 16) S. A. Moszkowski: Phys. Rev. **82** (1951) 35.
- 17) J. B. Gerhart, B. C. Carlson and R. Sherr: Phys. Rev. **94** (1954) 917.
- 18) F. Metzger: Phys. Rev. **101** (1956) 286; G. M. Temmer and N. P. Heydenburg: Phys. Rev. **94** (1954) 917.
- 19) E. L. Church and J. J. Kraushaar: Phys. Rev. **88** (1952) 419.
- 20) L. C. Biedenharn and M. E. Rose: Rev. Mod. Phys. **25** (1953) 746.
- 21) C. A. Mallmann: Phys. Rev. Letters **2** (1959) 507. M. Sakai: J. Phys. Soc. Japan **15** (1960) 933.
- 22) M. Sakai: Rep. Inst. Nucl. Study, University of Tokyo, INSJ-19 July (1959).
- 23) D. M. Van Patter: Nucl. Phys. **14** (1959/60) 42.
- 24) C. F. Coleman: Nucl. Phys. **7** (1958) 488.
- 25) S. S. Malik, V. R. Potnis and C. E. Mandeville: to be published.
- 26) R. K. Girgis and R. Van Lieshout: Physica **25** (1959) 688. C. Ythier, W. Schoo, B. L. Schram, H. L. Polak, R. K. Girgis, R. A. Ricci and R. Van Rieshout: Physica **25** (1959) 694.
- 27) E. Eichler, J. A. Marinsky, G. D. O'Kelley and N. R. Johnson: Bull. Amer. Phys. Soc. (1960) 10.

Theory of Formation Energy of the External and the Internal Surface for Free Electron Metals

By Akira SUGIYAMA

Nagoya Technical College, Nagoya

(Received December 19, 1959)

The formula for the surface energy $\sigma_S = k_F^4/160\pi$ is proved to be nearly valid for any self-consistent surface barrier, independently both of the surface shape and of the potential form.

1) On the basis of Friedel theorem and the extended expression $N(k) \simeq k^3 V/3\pi^2 - k^2 S/8\pi$ of Weyl-Laue theorem, it is proved that the formula $\sigma_S = k_F^4/160\pi$ holds not only for the plane surface but also for the surface of any shape, provided the surface potential barrier is infinitely high.

2) As the Friedel sum rule for the plane surface potential, the charge neutrality condition in the interior is obtained as

$$\int_0^{k_F} \eta(k_x) k_x dk_x = \frac{\pi k_F^2}{8}$$

in terms of the phase shift $\eta(k_x)$. Then the formula $\sigma = \beta \sigma_S$ for the surface energy is derived, where

$$\beta = \frac{80}{\pi} \frac{1}{k_F^4} \int_0^{k_F} \eta(k_x) k_x^3 dk_x - 5.$$

By these formulae, we can prove the approximate validity of σ_S (or $\beta \simeq 1$) for any self-consistent potential on the plane surface.

3) The surface energy of a small spherical cavity is calculated as a function of the radius, assuming the quasi self-consistent infinite barrier for the cavity surface.

4) The formation energy of an atomic vacancy and that of a vacancy pair are discussed as special cases of small volume cavities. The analysis shows the approximate validity of σ_S for any potential form.

§ 1. Introduction

The surface of metals is an interesting subject from theoretical point of view. The plane surface, one of the simplest imperfections, is a good example for us to test the validity of theoretical approaches. The consideration of surface of cavities reveals an intimate connection between theories of the plane surface and those of the atomic vacancy.

An imperfection in a metal is specified usually by a deformation in the lattice of positive ions. The perturbation potential of the imperfection, however, is not determined by the deformation alone, but also by the perturbation produced self-consistently in the free electrons.

Electron theories for imperfect lattices have been mainly developed for the point imperfection and the free plane surface, using the following three approaches:

(i) Thomas-Fermi approach. In spite of its success in the self-consistent treatment

of many-body problems¹⁾, the T-F approach fails in the self-consistent treatment of surface problems. The T-F approach leads to zero work function²⁾ and a negative surface energy³⁾.

(ii) Auxiliary potential approach. We make often use of a simple perturbation potential which gives an analytical solution of wave equations. The potential is fixed either by the observed work function³⁾ and the observed depth of conduction band⁴⁾, or by the theoretical requirement^{5), 6)} that the potential satisfies a condition for self-consistency. In the latter case a quasi self-consistent auxiliary potential is used.

(iii) Numerical approach. This approach was taken in the calculation of the formation energy of vacancy in copper^{7), 8)} and the plane surface energy of sodium⁹⁾. Although this approach is orthodox, it involves complicated numerical calculations for an individual metal and does not give results ready to be gener-

alized to other metals.

If a self-consistent perturbation potential is used for a localized imperfection, the perturbation in free electrons should be localized around the imperfection, and the region far from the imperfection should remain electrically neutral. Thus the charge neutrality is a necessary condition for the potential to be self-consistent. Friedel¹⁰⁾ has first pointed out the importance of the necessary condition and expressed the condition in a general form, proving Friedel theorem.

Applying his theorem to a point imperfection, he derived a useful rule, the Friedel sum rule, by which the heap up electrons around the imperfection is expressed in terms of the phase shift only. This rule was applied first by Fumi¹¹⁾ to the calculation of the formation energy of a vacancy. Friedel theorem is applicable to any other localized imperfection.

In this paper its application to the plane surface is discussed. The theorem gives a simple formula for the condition. In a special case, this formula is reduced to "the charge neutrality condition in the interior" given by the previous authors^{9), 12)}.

The main purpose of the present paper is to prove the approximate validity of the surface energy $\sigma_S = k_F^4/160\pi^*$ for any surface barrier, independently both of the boundary surface shape and of the potential barrier form. The verification is based on Friedel theorem, using the charge neutrality condition for the plane surface and the Friedel sum rule for the cavity. Previously the vacancy and the plane surface have been investigated independently. The present work connects the theory of the vacancy with that of the plane surface through the theory of the surface for the cavity.

§2. Surface Energy of the Infinite Wall

We assume a metal to be composed of the positive jelly¹²⁾ with uniform charge density ρ_0 , volume V_0 , and area of the boundary surface S_0 , and of a number $N_0 = \rho_0 V_0$ of elec-

trons moving free in a potential box.

We begin with the potential box enclosed by an infinitely high barrier, the infinite wall. The box has the volume V slightly different from V_0 and its boundary surface has the area $S \simeq S_0$. Following Huntington⁹⁾, the surface of the positive jelly is called geometrical and that of the potential box physical (see in Fig. 1).

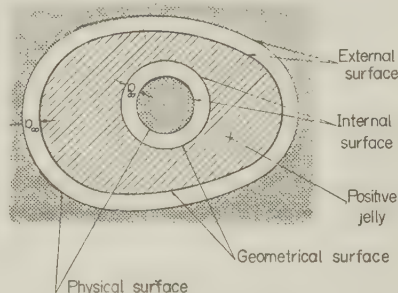


Fig. 1. Illustration of the geometrical, the physical, the internal, and the external surface. The hatching part shows the positive jelly, and the shading shows the infinitely high potential barrier.

2.1 An application of Friedel theorem and an extended expression of Weyl-Laue theorem to surface problems

As is well-known, the free electron is specified by wave number k related with the energy eigen value E_k by $E_k = k^2/2$.

The total number of electrons $N(k)$ within a given value of k is expressed formally by

$$N(k) \simeq \frac{k^3}{3\pi^2} V - \alpha k^2 S \quad (2.1)$$

to the order of k^2 . Now we do not impose any restriction on the shape of the positive jelly but its volume needs to be large. The first term represents the usual Weyl¹³⁾-Laue¹⁴⁾ theorem and the second is a correction term important in our discussion. The factor $k^2 S$ is obtained by the dimensional analysis and the numerical factor α is assumed to be

$$\alpha = 1/8\pi \quad (2.2)$$

for any shape, the validity of the assumption being discussed in §2.2.

Now the maximum wave number k_m is given by the relation

$$N(k_m) \simeq \frac{k_m^3}{3\pi^2} V - \alpha k_m^2 S = N_0 = \rho_0 V_0. \quad (2.3)$$

When we can neglect the surface effect at

* Atomic units $e = m = \hbar = 1$ are used throughout the paper, and then σ_S for monovalent metals is 0.01466 (ζ/r_S^2), where $\zeta = k_F^2/2$ is the usual Fermi level energy and r_S the Wigner-Seitz radius. The energy per one atom on the surface is given by $(k_F^4/160\pi) \cdot (\pi r_S^2) = 0.0460\zeta$.

all, k_m becomes the usual Fermi momentum k_F defined by

$$k_F = (3\pi^2 \rho_0)^{1/3} = 1.919 Z^{1/3} / r_S \tag{2.4}$$

with r_S the Wigner-Seitz radius of the Z -valent metals. In the following, however, we are concerned with monovalent metals except in § 6.4.

With Eq. (2.1), we can generalize some of characteristics of the surface, which have been obtained for the plane surface, to the surface with any shape without detailed calculations¹⁵⁾.

(i) Tendency of the infinite wall to expel free electrons

The density of the free electron gas $\rho(r)$ must be zero on the infinite wall and will increase to a constant ρ_i in the interior. A detailed analysis of $\rho(r)$ for the plane surface is carried out to higher order approximation in § 2.3. The results prove the validity of the T-F relation for the interior density ρ_i , to the first order of $S/Vk_m \simeq S_0/V_0k_F$;

$$\rho_i = k_m^3 / 3\pi^2, \tag{2.5}$$

which is written as

$$\rho_i = \frac{N_0}{V} + \frac{\alpha k_m^2 S}{V} \tag{2.6}$$

by using Eq. (2.3). The apparent excess charge $\alpha k_m^2 S \simeq k_F^2 S_0 / 8\pi$ over the average density N_0/V must cause the corresponding decrease in the surface region. Therefore, the infinite wall has the tendency to expel the free electrons into the interior by the amount $\alpha k_m^2 \simeq k_F^2 / 8\pi$ per unit area.

(ii) Quasi self-consistent location of the physical surface

We should have

$$\rho_i = \rho_0, \tag{2.7}$$

and then

$$k_m = k_F \tag{2.8}$$

to the first order of S_0/V_0k_F ; otherwise, an uncompensated charge distribution in the interior, even if as small as the first order of S_0/V_0k_F , causes an increase in energy proportional to the volume, besides the inconsistency with the initial assumption of the free electron. Eq. (2.7) expresses the charge neutrality in the interior and Eq. (2.8) expresses Friedel theorem.

Eq. (2.8), with Eq. (2.3), requires the relation

$$V = V_0 + \Delta V = V_0 + b_\infty S_0$$

with

$$k_F b_\infty = 3\pi^2 \alpha \tag{2.9}$$

or

$$b_\infty = \frac{3\pi}{8} \left(\frac{4}{9\pi} \right)^{1/3} r_S \simeq 0.641 r_S,$$

showing that the physical surface must be placed outward the geometrical surface by width b_∞ . Such physical surface should be called the quasi self-consistent infinite wall.

(iii) Surface energy

The total energy of the free electron gas is obtained by

$$E = \Sigma E_k = \int_0^{k_m} \frac{1}{2} k^2 \frac{\partial N(k)}{\partial k} dk = \frac{k_m^5}{10\pi^2} V - \frac{\alpha k_m^4}{4} S \tag{2.10}$$

to the first order of S_0/V_0k_F . Replacing k_m and V by surface-independent quantities k_F and V_0 given by Eqs. (2.8) and (2.9), we have

$$E = \frac{k_F^5}{10\pi^2} V_0 + \frac{\alpha k_F^4}{20} S_0,$$

the second term of which expresses the surface energy

$$\sigma_S = \alpha k_F^4 / 20 = k_F^4 / 160\pi \tag{2.11}$$

per unit area. This is a derivation generalized to any surface, internal or external, of the surface energy σ_S , which has been obtained for the plane surface by the previous authors^{9), 16)}. In the following, we take σ_F as the unit of the surface energy.

2.2 *Validity of the term $k^2 S / 8\pi$ in the extended expression of Weyl-Laue theorem and the surface energy of Brager and Schuchowitzky*

On the simple assumption $V = V_0$, we obtain

$$k_m = k_m^{(1)} \equiv k_F + \frac{\alpha \pi^2}{V_0} S_0 \tag{2.12}$$

from Eq. (2.3), and then rewriting Eq. (2.10) as

$$E = \frac{k_F^5}{10\pi^2} V_0 + \frac{\alpha k_F^4}{4} S_0,$$

we have the surface energy

$$\sigma^{(1)} = \alpha k_F^4 / 4. \tag{2.13}$$

On the other hand, the surface energy

$$\sigma^{(1)} = k_F^4 / 32\pi \tag{2.14}$$

has been obtained, on the same assumption $V = V_0$, by Feenberg¹⁷⁾ and by Brager and Schuchowitzky¹⁸⁾ for the plane surface, and

by Brager⁽¹⁰⁾ for the external surface of sphere.

The surface energy $\sigma^{(1)}$, called the Brager-Schuchowitzky surface energy, is only of a poor approximation from the physical point of view, because the assumption $V=V_0$ gives the excess interior density

$$\rho_i = \rho_i^{(1)} \equiv \frac{k_m^{(1)3}}{3\pi^2} = \rho_0 + \frac{\alpha k_F^2}{V_0} S_0 \quad (2.15)$$

over ρ_0 . Their investigations, however, serve both as a simple mathematical proof of $\alpha=1/8\pi$ and as a starting stage in the two-stage procedure taken later (§ 3).

(i) Validity of $\alpha=1/8\pi$

Comparing Eq. (2.13) with (2.14), we can prove $\alpha=1/8\pi$ immediately. In addition to the above investigations, we shall see in § 5.3 that the assumption $V=V_0$ leads to the surface energy $\sigma^{(1)}$ again for the internal surface of large spherical cavity. These examples prove the validity of $\alpha=1/8\pi$ for a surface whether its curvature is positive or negative or zero. Then we can take $\alpha=1/8\pi$ for any shape.

It is, however, desirable that the validity should be proved mathematically as an extension of Weyl-Laue theorem.

(ii) Role of starting surface energy

In the two-stage procedure, we start with the assumption $V=V_0$ and then replace the infinite wall on the geometrical surface by a more reasonable potential barrier so that the charge neutrality is satisfied.

The quasi self-consistent infinite wall is obtained also as one of the simplest examples of this procedure. In the starting stage we obtain $\sigma^{(1)}$ and $\rho_i^{(1)}$. And then we expand the infinite wall uniformly by an amount b normal to the surface so that $\rho_i = \rho_0$. Since $V = V_0 + bS_0$ and

$$\rho_i = \rho_i^{(1)} \cdot \frac{V_0}{V} = \rho_0 + \frac{k_F^2}{3\pi^2} \frac{S_0}{V_0} (3\pi^2 \alpha - k_F b),$$

the condition $\rho_i = \rho_0$ determines $b = b_\infty$. The expansion of the electron gas reduces the total kinetic energy ΔE_e by an amount proportional to surface area

$$\Delta E_e/E \simeq -(2/3)(\Delta V/V_0) = -(2/3)(b_\infty S_0/V_0)$$

$$\therefore \Delta E_e = \sigma_e \cdot S_0 \quad \text{with} \quad \sigma_e = -\alpha k_F^4/5.$$

Therefore the total surface energy is again

$$\sigma = \sigma^{(1)} + \sigma_e = \frac{\alpha}{20} k_F^4 = \sigma_S.$$

2.3 Illustration of the plane surface of the infinite wall

To see the validity of $\alpha=1/8\pi$ and the behaviour $\rho(r)$ explicitly, we consider a metal with a finite thickness L_0 in x -direction and infinite breadth in y and z directions, and take the surface potential

$$V(r) = V(x) = 0; \quad 0 \leq x \leq L \\ = \infty; \quad \text{otherwise.} \quad (2.16)$$

Under the cyclic boundary condition of length L_1 in y and z directions, we have the wave function

$$\psi(\mathbf{k}, \mathbf{r}) = \chi(k_x, x) \cdot (1/L_1) \cdot \exp i(k_y y + k_z z) \\ \chi(k_x, x) = (2/L)^{1/2} \cdot \sin k_x x; \quad 0 \leq x \leq L \\ = 0; \quad \text{otherwise} \quad (2.17)$$

and the quantum relation $\mathbf{k} = \mathbf{k}(n)$;

$$k_x = k_x(n_x) = \pi n_x / L; \quad n_x = 1, 2, \dots, n_m, \dots \\ k_y = k_y(n_y) = 2\pi n_y / L_1; \quad n_y \left. \begin{array}{l} \\ \end{array} \right\} 0, \pm 1, \pm 2, \dots \\ k_z = k_z(n_z) = 2\pi n_z / L_1; \quad n_z \left. \begin{array}{l} \\ \end{array} \right\} 0, \pm 1, \pm 2, \dots \quad (2.18)$$

The quantities, obtained when we put $L=L_0$, are superscribed by (1) as $V^{(1)}(x)$, $\psi^{(1)}$, $\chi^{(1)}$, $\mathbf{k}^{(1)}(n)$, etc., which are taken as the starting of the two-stage procedure in § 3.1.

The state of the free electron is represented by the lattice point in $\mathbf{k}$ -space. At $0^\circ K$, the total occupied states form the positive half of k_x of the so-called the Fermi sphere with the radius k_m in $\mathbf{k}$ -space.

The total number of the occupied states within k_m is given

$$N(k_m) = \frac{L_1^2}{2\pi} \sum_{n_x}^{n_m} \{k_m^2 - k_x^2(n_x)\} \\ = \frac{k_m^3}{3\pi^2} L_1^2 L - \frac{k_m^2}{4\pi} L_1^2 - \frac{k_m}{12} \frac{L_1^2}{L} \\ = N_0 = \frac{k_F^3}{3\pi^2} L_1^2 L_0. \quad (2.19)$$

Since only the terms of the first order of $S_0/V_0 k_F = 1/L_0 k_F$ are important, Eq. (2.19) is simplified to the extended Weyl-Laue theorem

$$N(k_m) = \frac{k_m^3}{3\pi^2} V - \frac{k_m^2}{8\pi} S \quad (2.20)$$

with $V = L_1^2 L$ and $S = 2L_1^2$. This proves $\alpha = 1/8\pi$ for the plane surface.

The density of the electron gas is expressed analytically as

$$\begin{aligned}
 \rho(r) &= \sum_k |\psi(k, r)|^2 \\
 &= \frac{1}{2\pi} \sum_{n_x} |\chi(k_x, x)|^2 (k_m^2 - k_x^2(n_x)) = \rho(x) \\
 &= \frac{k_m^3}{3\pi^2} \left[1 - \frac{1}{4} \left(\frac{\pi}{Lk_m} \right)^2 \left\{ 1 - \frac{3 \cos(2k_mx)}{\sin^2(\pi x/L)} \right\} \right. \\
 &\quad \left. - \frac{3}{8} \left(\frac{\pi}{Lk_m} \right)^3 \left\{ \frac{\cos(\pi x/L) \sin(2k_mx)}{\sin^3(\pi x/L)} \right\} \right]. \quad (2.21)
 \end{aligned}$$

Except in the vicinity of the surface $|x/L| \ll 1$ or $|1 - (x/L)| \ll 1$, $\rho(x)$ is simplified to the constant interior density to the first order of $1/L_0 k_F$ as

$$\rho(x) \rightarrow \rho_i = \frac{k_m^3}{3\pi^2} = \frac{N_0}{V} + \frac{k_F^2}{4\pi L}. \quad (2.22)$$

Eq. (2.22) proves the higher order validity of T-F relation and the tendency to expel $k_F^2/8\pi$ electrons per unit area of the infinite wall, because $(k_F^2/4\pi L) \cdot V = (k_F^2/8\pi) \cdot S$.

In the vicinity of the surface, $\rho(x)$ is simplified to

$$\rho(x) \simeq \rho_i \{1 - g(2k_F x)\}$$

with

$$g(t) = 3(\sin t - t \cos t)/t^3. \quad (2.23)$$

This formula agrees with that derived by Swiatecki¹⁶⁾, except ρ_i for ρ_0 , and is shown in Fig. 2. Although the approximation made in its derivation is no longer valid for larger $k_F x$, Eq. (2.23) holds higher order validity, because

$$\rho_i \int_0^\infty g(2k_F x) dx = k_F^2/8\pi.$$

We define the region $0 \leq x \leq b_s (\simeq 5r_s)$, in

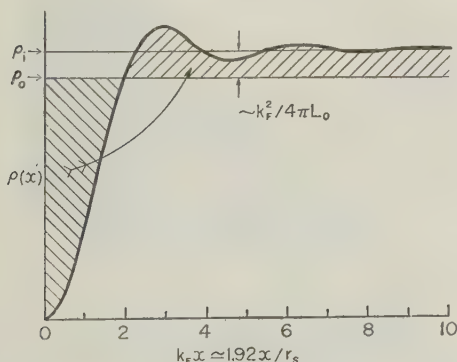


Fig. 2. Density $\rho(x)$ of the free electron gas for the infinite wall which is placed on the geometrical surface is shown as a function of the distance from the surface. ρ_i and ρ_0 show the interior (constant) and the positive jelly density, respectively.

which $\rho(x)$ deviates considerably from the T-F density $\rho_i = k_m^3/3\pi^2$, as the surface thickness, although the numerical value is chosen somewhat arbitrarily. In the discussion of surfaces, the behaviour of electrons in the surface thickness is important. This is a reason why the T-F approach fails in the self-consistent treatment of surfaces. b_s shows the depth of the effect of the infinite wall on the electron density in the free space and then is a measure of the applicable range of Friedel theorem for a thin metallic film.

§ 3. Plane Surface Energy of the Self-Consistent Potential

The infinite wall, even if quasi self-consistent, is of a rough approximation to an actual surface potential, which cannot be infinite nor discontinuous.

3.1 Fundamental formulae for the surface potential

As the starting stage, we take the infinite wall $V^{(1)}(x)$, and obtain the wave function $\psi^{(1)}$, the surface energy $\sigma^{(1)}$ and the excess density $\rho^{(1)}_i$. Then we replace $V^{(1)}(x)$ by another potential $V^{(*)}(x)$, and obtain the wave function

$$\psi^{(*)}(k, r) = \{1 + \delta(k_x)\} \chi^{(*)}(k_x, x) \cdot (1/L_1) \cdot \exp i(k_y y + k_z z) \quad (3.1)$$

$$\delta(k_x) = -\frac{1}{L_0} \frac{\partial \eta(k_x)}{\partial k_x} \quad (3.2)$$

where $\eta(k_x)$ is the phase shift defined by the asymptotic behaviour

$$\chi^{(*)}(k_x, x) \rightarrow (2/L_0)^{1/2} \sin \{k_x x + \eta(k_x)\}$$

in the interior. We assume that the potential $V^{(*)}(x)$ traps no electrons in the surface region that is

$$\eta(0) = 0. \quad (3.3)$$

The density $\rho^{(*)}(x)$ is complicated in the surface region, but becomes a constant $\rho_i^{(*)}$ given by

$$\begin{aligned}
 \rho_i^{(*)} &= \rho_i^{(1)} + \frac{1}{2\pi^2} \int_0^{k_F} \delta(k_x) (k_F^2 - k_x^2) dk_x \\
 &= \rho_0 + \frac{2}{\pi^2 L_0} \left\{ \frac{\pi}{8} k_F^2 - \int_0^{k_F} \eta(k_x) k_x dk_x \right\} \quad (3.4)
 \end{aligned}$$

in the interior. Eq. (3.4) is derived also by summing Eq. (3.1) with the asymptotic form for $\chi^{(*)}$.

The detailed discussions of Eqs. (3.2), (3.4)

are closely related with a rigorous derivation of Friedel theorem, and will be given in the later paper with the definition of the Fermi momentum $k_m^{(*)}$ in the perturbed electron gas.

The charge neutrality $\rho_i=\rho_0$ in Eq. (3.4) gives

$$\int_0^{k_F} \eta(k_x) k_x dk_x = \frac{\pi}{8} k_F^2. \quad (3.5)$$

The change in energy of the free electron produced by the replacement is also described by the phase shift only. The symmetry of $\chi^{(*)}$ about $x_c=L_0/2$ yields the quantum condition

$$k_x^{(*)}(n_x) \cdot \frac{L_0}{2} + \eta(k_x^{(*)}(n_x)) = \frac{\pi}{2} n_x = k_x^{(1)}(n_x) \frac{L_0}{2}. \quad (3.6)$$

Therefore the quantum value $k_x^{(1)}$ is displaced to

$$k_x^{(1)} \rightarrow k_x^{(*)} = k_x^{(1)} + \Delta k_x$$

with

$$\begin{aligned} \Delta k_x &= -\frac{2}{L_0} \eta(k_x^{(*)}(n_x)) \\ &\simeq -\frac{2}{L_0} \eta(k^{(1)}(n_x)) = -\frac{2}{L_0} \eta(k_x). \end{aligned}$$

Summing up the change in energy $k_x^{(1)} \Delta k_x$ over the Fermi distribution, we obtain the energy change ΔE_p proportional to the surface area

$$\Delta E_p = \sigma_p \cdot S_0$$

with

$$\sigma_p = -\frac{1}{2\pi^2} \int_0^{k_F} k_x \cdot \eta(k_x) \cdot (k_F^2 - k_x^2) dk_x, \quad (3.7)$$

and then the total surface energy

$$\sigma^{(*)} = \sigma^{(1)} + \sigma_p = \beta \sigma_S$$

with

$$\beta = 5 - \frac{80}{\pi} \frac{1}{k_F^4} \int_0^{k_F} \eta(k_x) k_x (k_F^2 - k_x^2) dk_x. \quad (3.8)$$

Furthermore, when $\eta(k_x)$ satisfies the charge neutrality (3.5), we can simplify Eq. (3.8) to

$$\beta = \frac{80}{\pi} \frac{1}{k_F^4} \int_0^{k_F} \eta(k_x) k_x dk_x - 5. \quad (3.9)$$

3.2 General survey of the plane surface energy

β seems sensitive to a form of the surface potential, for Eq. (3.9) is expressed by subtracting two large quantities. β for any self-consistent surface potential, however, cannot deviate so widely from 1.0,

Since $\eta(0)=0$, $\eta(k_x)$ may be expanded in a Taylor series

$$\eta(k_x) \simeq C_1(k_x/k_F) + C_2(k_x/k_F)^2, \quad (3.10)$$

without any detailed knowledge about the surface potential but the repulsive potential.

The condition (3.5), applied to Eq. (3.10), requires the relation

$$\frac{C_1}{3} + \frac{C_2}{4} = \frac{\pi}{8}. \quad (3.11)$$

The formula (3.9) gives the surface energy $\sigma=\beta\sigma_S$ with

$$\beta = \frac{80}{\pi} \left(\frac{C_1}{5} + \frac{C_2}{6} \right) - 5,$$

and then

$$= \frac{5}{3} - \frac{16}{9} \frac{C_1}{\pi} = 1 + \frac{4}{3} \frac{C_2}{\pi} \quad (3.12)$$

with Eq. (3.11).

There are restrictions on the allowed range of C_1 and C_2 . First $\partial\eta/\partial k_x$ should not be a monotonously decreasing function of k_x ; for the probability of an electron being found outside the geometrical surface is proportional to $\partial\eta/\partial k_x$, and should not decrease with energy. Secondly $\eta(k_x)$ will also be a monotone-

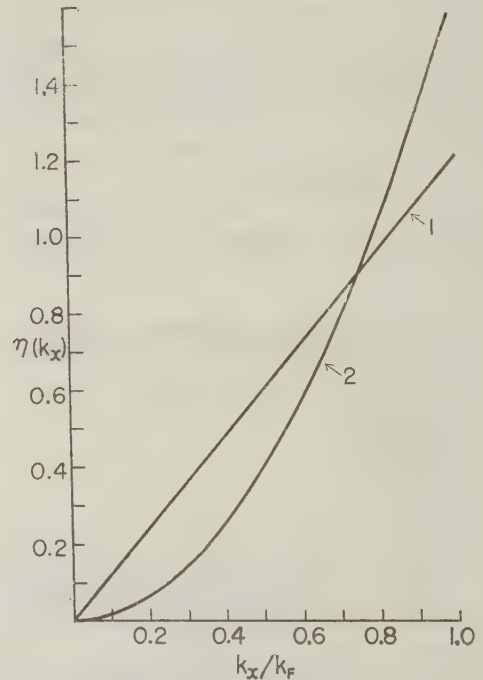


Fig. 3. Typical behaviours of the phase shift $\eta(k_x)$ as functions of k_x ; curve 1 represents $\eta(k_x)$ for $C_1=3\pi/8$, $C_2=0$ and then $\beta=1.0$, and curve 2 represents $\eta(k_x)$ for $C_1=0$, $C_2=\pi/2$ and then $\beta=5/3$.

ously increasing function of k_x ; for, when taking the approximation of cutting the Taylor expansion down to the only first two terms, we implicitly assume the predominancy of the linear term.

Therefore we obtain

$$\frac{3\pi}{8} \geq C_1 > 0, \quad \frac{\pi}{2} > C_2 > 0,$$

and then

$$\frac{5}{3} > \beta \geq 1. \tag{3.13}$$

In Fig. 3, we show two curves of $\eta(k_x)$ for the limiting cases $C_1=3\pi/8, C_2=0$; and $C_1=0, C_2=\pi/2$, corresponding values of β being 1.0 and 5/3, respectively. These curves are good approximations to those of $\eta(k_x)$ shown in Fig. 5, which are calculated for various forms for the potential barrier. The approximation proves the reasonablity of the Taylor expansion.

§ 4. Application to Several Forms for the Plane Surface Potential Barrier

We are now ready to discuss the theories of surface energy given by several authors

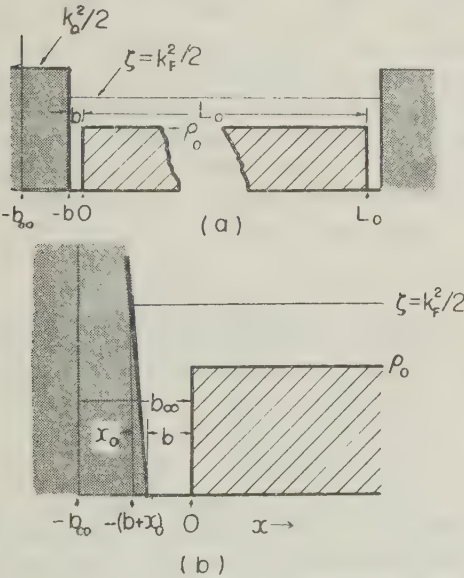


Fig. 4. Schematic illustration of surface potentials. (a) the step potential barrier of height $k_0^2/2$ at b outward the geometrical surface. (b) the linear potential barrier with a slope parameter $k_F x_0$ and the displacement b . The hatching part shows the positive jelly and the shading shows the potential barrier.

by applying our formulae (3.5), (3.9).

4.1 Quasi self-consistent treatment of the finite step potential

We consider the step potential barrier with a finite height $k_0^2/2$ just outside the geometrical surface. The barrier produces the phase shift

$$\eta(k_x) = \sin^{-1}(k_x/k_0). \tag{4.1}$$

Our formulae determine

$$k_0 = k_F, \quad \text{and then } \beta = 1.25. \tag{4.2}$$

In order to take an arbitrary value for k_0 , we should introduce another adjustable parameter; we have only to displace the step potential barrier rigidly by b outward, as shown in Fig. 4(a). The displaced potential produces the phase shift

$$\eta_C(k_x) = \sin^{-1}(k_x/k_0) + k_x b. \tag{4.3}$$

The charge neutrality (3.5) requires the relation between b and k_0

$$\frac{2}{3} k_F^3 b = \frac{\pi}{4} k_F^2 + \frac{1}{2} (k_0^2 - 2k_F^2) \sin^{-1}\left(\frac{k_F}{k_0}\right) - \frac{1}{2} k_F \sqrt{k_0^2 - k_F^2}, \tag{4.4}$$

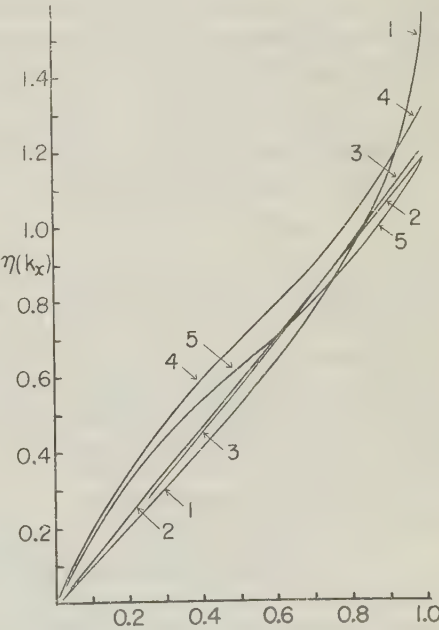


Fig. 5. Behaviours of $\eta(k_x)$ for several (quasi) self-consistent potential barriers; curve 1, 2 represent the step potential barrier with $k_0 = k_F$ and $k_0 = 2k_F$, respectively; curve 3 the linear potential barrier with the slope parameter $k_F x_0 = 0.5533$, for which $b = 0$; curve 4 the Huntington's $\eta(k_x)$ of Eq. (4.13), while curve 5 is the corrected phase shift Eq. (4.14).

which reduces to Eq. (2.9), say $k_F b = 3\pi/8$, as $k_0 \rightarrow \infty$, and to Eq. (4.2), say $b=0$, as $k_0 \rightarrow k_F$. The typical behaviours of $\eta(k_x)$ for $k_0=k_F$ and $k_0=2k_F$ are shown in curve 1 and 2 in Fig. 5, respectively. The relation (4.4) agrees with "the charge conservation law"* introduced by Bardeen⁵⁾.

Formula (3.9), combined with Eq. (4.4), gives the surface energy

$$\beta = 1 - \frac{4}{\pi} \left\{ 1 - 3 \left(\frac{k_0}{k_F} \right)^2 + \frac{15}{8} \left(\frac{k_0}{k_F} \right)^4 \right\} \sin^{-1} \left(\frac{k_F}{k_0} \right) - \frac{1}{\pi} \left\{ \left(\frac{k_0}{k_F} \right)^2 - 1 \right\}^{1/2} \cdot \left\{ 7 - \frac{15}{2} \left(\frac{k_0}{k_F} \right)^2 \right\}, \quad (4.5)$$

which agrees with the results given by Huntington⁹⁾, giving 1.0 for $k_0 \rightarrow \infty$, and 1.25 for $k_0=k_F$.

Although the application cannot bring new results in this case, the results given by previous authors are obtained on a firmer basis as simple examples for our formulae.

In this connection, we shall discuss a convenient method of correcting a potential, the phase shift of which does not satisfy the condition (3.5); we have only to displace the potential rigidly outward by b so that the displaced phase shift

$$\eta_c(k_x) = \eta(k_x) + k_x b \quad (4.6)$$

may satisfy the condition (3.5). And we have

$$k_F b = 3 \left\{ \frac{\pi}{8} - \frac{1}{k_F^2} \int_0^{k_F} \eta(k_x) k_x dk_x \right\},$$

or

$$b/b_\infty = 1 - \left\{ \int_0^{k_F} \eta(k_x) k_x dk_x / (\pi k_F^2/8) \right\}. \quad (4.7)$$

Such correction may be called a correcting displacement. The surface energy β is expressed in terms of $\eta_c(k_x)$ and then, eliminating b by Eq. (4.7), in terms of $\eta(k_x)$;

$$\beta = 1 + \frac{80}{\pi} \frac{1}{k_F^4} \left\{ \int_0^{k_F} \eta(k_x) k_x^3 dk_x - \frac{3}{5} k_F^2 \int_0^{k_F} \eta(k_x) k_x dk_x \right\}, \quad (4.8)$$

which is regarded as a generalization of Eq. (3.9) to any surface potential, whether the phase shift satisfies the charge neutrality or not. Eq. (4.8) is a simple, analytical expression for Swiatecki's¹⁶⁾ formula of the (nuclear)

surface energy, which is expressed in terms of the kinetic and the potential energy density. An application to the nuclear surface energy will be discussed later.

Eqs. (4.4), (4.5) are obtained also as examples of the formulae (4.7), (4.8).

4.2 Quasi-consistent treatment of linear potential barrier

The linear potential barrier, the left hand side of which is expressed as

$$V(x) = \frac{k_F^2}{2} \frac{x}{(-x_0)} = -\xi x/x_0; \quad x < 0 \\ = 0; \quad \text{otherwise}$$

has been investigated by Swiatecki¹⁶⁾. We have the phase shift

$$\eta(k_x) = F(\omega) \\ = \tan^{-1} [\{J_{1/3}(\omega) + J_{-1/3}(\omega)\} / \{J_{-2/3}(\omega) - J_{2/3}(\omega)\}], \quad (4.9)$$

with

$$\omega = \theta \cdot (k_x/k_F)^3,$$

$$\theta = (2/3)(k_F x_0),$$

J_ν ; the Bessel function of order ν .

Although he considered the slope parameter $k_F x_0$ adjustable, our formulae determine

$$k_F x_0 = 0.5533, \quad \text{and then } \beta = 1.054 \quad (4.10)$$

uniquely. $\eta(k_x)$ with this value of $k_F x_0$ is shown as curve 3 in Fig. 5.

In order to make $k_F x_0$ an adjustable parameter, we may introduce another parameter, the correcting displacement b , as shown in Fig. 4(b). With Eqs. (4.6) and (4.7) we obtain

$$\eta_c(k_x) = F(\omega) + k_x b$$

with

$$k_F b = 3 \left\{ \frac{\pi}{8} - \frac{1}{3\theta^{2/3}} \int_0^\theta F(\omega) \omega^{-1/3} d\omega \right\}, \quad (4.11)$$

and

$$\beta = 1 + \frac{80}{\pi} \left[\frac{1}{3\theta^{4/3}} \int_0^\theta F(\omega) \omega^{1/3} d\omega - \frac{1}{5\theta^{2/3}} \int_0^\theta F(\omega) \omega^{-1/3} d\omega \right]. \quad (4.12)$$

For small $k_F x_0$,

$$\beta \simeq 1 + \frac{64}{35\pi} \left[1 - \frac{1}{9} \{ \Gamma(1/3)/\Gamma(2/3) \}^8 \right] k_F x_0 \\ = 1 + 0.08128 k_F x_0. \quad (4.12')$$

Eq. (4.12') is an analytical expression for the numerical result given by Swiatecki¹⁶⁾, and Eq. (4.12) is a quantitative expression for the qualitative result suggested by him²⁰⁾. The

* His naming seems improper, for it may result from his wrong use of the normalization factor.

results of numerical calculation for b and β are shown in Fig. 6(a) and (b), respectively. The values given in Eq. (4.10) are obtained by setting $b=0$ in these figures.

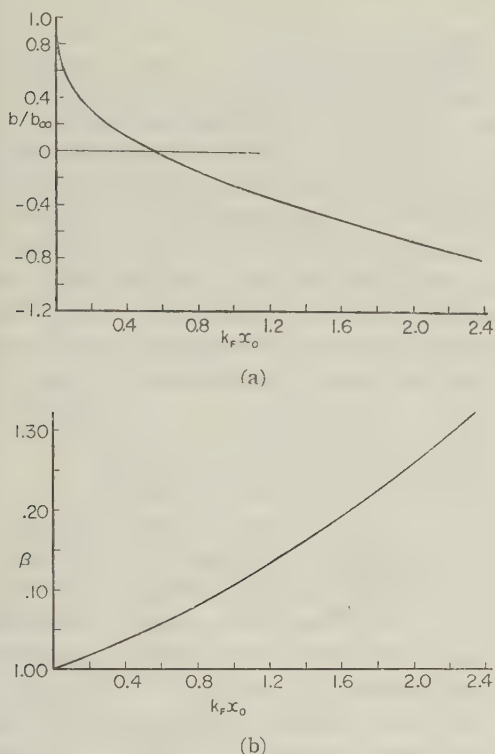


Fig. 6. Results of the numerical calculation for the quasi self-consistent linear potential barrier. (a) b/b_∞ is given as a function of the slope parameter $k_F x_0$. (b) β is given as a function of the slope parameter $k_F x_0$.

4.3 Analysis of the self-consistent potential for sodium by Huntington

The self-consistent surface potential is determined by the coulomb interaction due to an uncompensated charge distribution in the surface region.

The interaction is analyzed usually into three parts; the average electrostatic, the spin-dependent exchange and the correlation interaction. It is very complicated even on the simplest model to calculate each interaction potential so as to be consistent with itself and with the other two. There is, however, an approach taken by Bardeen⁵⁾ and later by Huntington⁹⁾, who found that the exchange and the correlation potential do not depend so sensitively on the distribution of electrons in the surface region as the average electro-

static potential. In Bardeen's theory of the work function of sodium, the surface potential depends on k . Huntington, following Bardeen, has made further simplification that the potential for the fixed value, $k_x = 0.8k_F$, $k_y = k_z = 0$, may be regarded, to a good approximation, as a common potential to all electrons.

Huntington obtained the phase shift

$$\eta(k_x) = k_x r_s [0.66 + 0.7\{0.8 - (k_x/k_F)\}^2] \quad (4.13)$$

and the surface energy

$$\beta = 0.41$$

for his self-consistent potential.

Since the potential in his approximation is a function of k_x only, the previous formulae are applicable*. But Eq. (4.13) gives

$$\int_0^{k_F} \eta(k_x) k_x dk_x = 1.12 \cdot (\pi k_F^2/8)$$

inconsistent with Eq. (3.5). This shows existence of some errors in his calculation, which might be caused by a lack of care in the normalization procedure**.

His potential should be corrected by the previous method of correcting displacement. We should, however, be careful in the direct application of the method; for the self-consistent barrier cannot be displaced rigidly. Huntington's potential, when displaced outward by b , produces the phase shift

$$\eta_c(k_x) = \eta(k_x) + k_x b + \Delta\eta,$$

where $\Delta\eta$ represents the effect of deformation of the potential produced by the displacement on $\eta(k_x)$. For small $k_x b$, we may expect

$$\Delta\eta \simeq \mu \cdot k_x b$$

with μ a numerical factor, because $\Delta\eta=0$ for $k_x=0$ by the assumption (3.3) and for $b=0$ by the definition. Therefore, when we are sure that the deformation is small, we can apply the method of correcting displacement by taking the effective displacement

* When the surface potential depends also on k , the phase shift η is a function of k_x , k_y , k_z . Therefore we should modify our formulae. The modification will be discussed in the later paper.

** He did not normalize the charge of each electron but normalized the total density ρ_i of electron gas in the interior so that $\rho_i = \rho_0$. The difference between ρ_i and ρ_0 , even if it exist, is too small to be computed by a numerical calculation directly.

$$b_0 = (1 + \mu)b$$

for b in the previous formulae.

The deformation of Huntington's potential is considered to be small for the following reasons. The displacement cannot cause any considerable change in the form of the average electrostatic potential, because his potential is calculated as if ρ_i were equal to ρ_0 exactly. The displacement justifies the basis of his calculation for the average potential. The exchange and the correlation potential are affected by the displacement, but produced changes in these potentials would be small in the interior for the similar reason to the average potential. Outside the geometrical surface, an image type interaction is predominant of the three, and this is insensitive to a small change in the surface region. Considering other approximations made by him, we can say that the deformation is small.

The phase shift thus corrected is

$$\eta_C(k_x) = k_x r_s [0.586 + 0.7 \{0.8 - (k_x/k_F)\}^2]$$

with

$$b_0 = -0.12b_\infty = -0.074r_s. \quad (4.14)$$

And the surface energy $\beta\sigma_s$ is given as

$$\beta = 0.87. \quad (4.15)$$

Curve 4 and 5 show the uncorrected and the corrected phase shift, Eq. (4.13) and (4.14), respectively. The correction is rather small in the phase shift but large in the surface energy.

Huntington has corrected the errors both of counting twice the interaction between free electrons and of neglecting cell structures. According to him, these corrections contribute 0.16 to β . Therefore the total surface energy is

$$\beta = 1.03,$$

whereas Huntington's is $\beta = 0.57$.

The close agreement with the simplified model of the quasi self-consistent infinite wall will result from a fortuitous fact that the exchange and the correlation energy neglected in the simplified model are nearly compensated by overestimation of counting twice the interaction between electrons.

§ 5. Dependence of Spherical Surface Energy on its Radius

So far we have seen $\beta \simeq 1$ independently

both of the surface shape of the infinite wall and of the potential form on the plane surface. Now we discuss effects of the curvature of the surface on the surface energy explicitly.

5.1 Spherical metal

We start with a spherical metal with a given radius R_0 . This is approximated by the free electron gas in a spherical box with radius R enclosed by the quasi self-consistent infinite wall. Therefore the radial part of the wave function is the Bessel function of the order of half-integer $J_{l+1/2}(k \cdot r)$, and k is quantized to be $k_{l,m} = x_{l,m}/R$, where $x_{l,m}$ is the m -th root $J_{l+1/2}(x_{l,m}) = 0$.

The total energy $E(R) = \Sigma(k_{l,m}^2/2)$ is rewritten as

$$\begin{aligned} E(R) &= \frac{4\pi}{3} R_0^3 \cdot \rho_0 \left(\frac{3}{5} \zeta \right) + 4\pi R_0^2 \cdot \sigma \\ &= \frac{2}{15\pi} k_F^5 R_0^3 + \frac{\beta}{40} k_F^4 R_0^2 \end{aligned} \quad (5.1)$$

and we obtain the surface energy $\sigma = \beta\sigma_s$ as a function of radius R_0 , if only we know the relation between R and R_0 .

For a larger radius, R should be determined by the charge neutrality condition in the interior and then the previous discussion gives $R = R_0 + b_\infty$ and $\beta = 1$, nearly independently of R_0 .

For small radius, β may depend on R_0 , although actual calculations involve the same difficulty as the calculations of the thin metallic film do. A criterion for the small radius is $R_0 \simeq 4.8b_s$, for which the volume of the surface thickness is equal to that of the interior. Assuming the previous value $b_s \simeq 5r_s$ even for the spherical surface, we can estimate $R_0 \simeq 24r_s$.

In metal physics the surface effect of a small spherical box absorbs less interests and requires more complicated calculations than that of a small cavity does. But the effect may be important to the theory of nuclear surface, because $R_0 > R_0$ for any real nucleus.

5.2 Spherical cavity

The formation energy ΔE of a cavity of macroscopic scale is chiefly required to form an internal surface in metals. And we define

the (apparent) surface energy* σ as $\Delta E/S_0$, where S_0 is the area of the geometrical surface of the cavity, even for a cavity of microscopic scale.

We start with a spherical metal with a sufficiently large radius R_0 . The effect of the outer surface, which is now not interesting, is approximated by the quasi self-consistent infinite wall with radius $R=R_0+b_\infty$. Then we introduce a cavity with the geometrical radius a_0 at the center of the metal.

The formation produces an expansion of the external radius by ΔR_0 in order to conserve the total volume of the positive jelly, and produces perturbation on the wave function so that its radial part is

$$f_l(r) = J_{l+1/2}(kr) - (-)^{l+1} \tan \eta_l(k) \cdot J_{-(l+1/2)}(kr) \quad (5.2)$$

with η_l the phase shift, besides the change in the normalization factor.

The boundary condition on the outer sphere $f(R+\Delta R_0)=0$ determines the change in the quantized value $k'_{l,m}=k_{l,m}+\Delta k$;

$$\Delta k = \Delta k_e + \Delta k_p$$

with

$$\begin{aligned} \Delta k_e &= -k \cdot (\Delta R_0/R) \\ \Delta k_p &= -\eta_l(k)/R \cdot \sin \tau; \quad \cos \tau = (l + \frac{1}{2})/R \cdot k, \end{aligned} \quad (5.3)$$

because the boundary condition is simplified to

$$\cos \left\{ (l + \frac{1}{2})(\tan \tau' - \tau') - \frac{\pi}{4} + \eta_l \right\} = 0$$

$$k'_{l,m} = k_{l,m} + \Delta k = (l + \frac{1}{2})/(R + \Delta R_0) \cos \tau'$$

by using Debye's asymptotic formulae^{(21), (22)}

$$\begin{aligned} J_\nu(\nu \cdot \sec \tau) \\ \sim \cos \left\{ \nu(\tan \tau - \tau) - \frac{\pi}{4} \right\} / \sqrt{\frac{\pi}{2} \nu \tan \tau} \end{aligned}$$

* In the classical treatment⁽³¹⁾, the formation energy $\Delta E(a_0)$ of a spherical cavity with radius a_0 in an elastic medium with rigidity modulus G is given as

$$\begin{aligned} \Delta E(a_0) &= 4\pi a_0^2 \cdot \sigma_0 \cdot \{1 + (\delta/k_F a_0)\}^{-1}, \\ \delta &= \frac{1}{2} \left(\frac{9\pi}{4} \right)^{1/3} \frac{\sigma_0}{G r_s} \end{aligned}$$

with σ_0 the surface [energy for the plane. Then we have

$$\sigma = \beta' \sigma_0, \quad \beta' = \{1 + (\delta/k_F a_0)\}^{-1}$$

as function of $k_F a_0$. δ varies with metals from 0.2 for copper to 0.6 for sodium. β' should be compared with Eq. (5.24).

$$Y_\nu(\nu \cdot \sec \tau)$$

$$\sim \sin \left\{ \nu(\tan \tau - \tau) - \frac{\pi}{4} \right\} / \sqrt{\frac{\pi}{2} \nu \tan \tau}. \quad (5.4)$$

Therefore the change in the total energy consists of two terms

$$\Delta E = \Delta E_e + \Delta E_p$$

with

$$\begin{aligned} \Delta E_e &= \sum_{l,m} 2(2l+1) \cdot k_{l,m}^3 \cdot (-\Delta R_0/R) \\ &= -4k_F^5 R^2 \Delta R_0/15, \\ \Delta E_p &= \sum_{l,m} 2(2l+1) \cdot k_{l,m} \cdot \{-\eta_l(k)/R \sin \tau\} \\ k &= (l + \frac{1}{2})/R \cos \tau. \end{aligned} \quad (5.5)$$

Since the increase in the total surface area is effectively $4\pi a_0^2$, the surface energy $\sigma = \beta \sigma_s$ is defined by

$$\Delta E(a_0) = 4\pi a_0^2 \sigma = \beta k_F^4 a_0^2/40. \quad (5.6)$$

The value of ΔR_0 and the phase shift η_l are connected with a_0 through the charge Q expelled with the formation of the cavity. We have

$$Q = \frac{4\pi}{3} a_0^3 \rho_0 = \frac{4}{9\pi} k_F^3 a_0^3 \quad (5.7)$$

as the expelled positive jelly, and

$$\begin{aligned} Q &= 4\pi R_0^2 \Delta R_0 \cdot \rho_0 \\ &= \frac{4}{3\pi} k_F^3 R_0^2 \Delta R_0 \simeq \frac{4}{3\pi} k_F^3 R^2 \Delta R_0 \end{aligned} \quad (5.8)$$

as the expansion of the outer surface. On the other hand, the Friedel sum rule gives

$$Q = -\frac{2}{\pi} \sum_l^\infty (2l+1) \eta_l(k_F) \quad (5.9)$$

as the number of the expelled free electrons.

With Eqs. (5.7), (5.8), ΔE_e is easily rewritten as

$$\Delta E_e = -\frac{4}{45\pi} k_F^5 a_0^3 = -\frac{2}{5} \xi \cdot Q, \quad (5.10)$$

independently of the details of the perturbation potential.

For the calculation of ΔE_p , we can use the approximate summation

$$\sum_l^{k_F R} (2l+1) (\eta_l/\sin \tau) \simeq \sum_l^{k_F a_0} (2l+1) \eta_l \simeq \sum_l^\infty (2l+1) \eta_l, \quad (5.11)$$

because η_l with $l > k_F a_0$ [are small and yet $a_0 \ll R$ so that we have only to take terms with $\sin \tau = 1$ into account. Further calculation requires a detailed knowledge of the potential form.

5.3 Cavity with the infinite wall

We begin with the quasi self-consistent infinith wall on the physical surface with radius a . Now the phase shift η_l is determined by the boundary condition on the (internal) physical surface:

$$\tan \eta_l(ka) = (-)^{l+1} J_{l+1/2}(ka) / J_{-(l+1/2)}(ka). \quad (5.12)$$

(i) Cavity with large radius

We consider the cavity with $a_0 \gg r_s$ to show $\sigma \rightarrow \sigma_s$ as $a_0 \rightarrow \infty$. Now we can obtain an approximate expression of η_l as a function of ka , by applying Debye formulae to Eq. (5.12);

$$\begin{aligned} -\eta_l(ka) &\simeq (l + \frac{1}{2})(\tan \kappa - \kappa) + \frac{\pi}{4} \\ \cos \kappa &= (l + \frac{1}{2})/ka \quad ; \quad \text{for } l < ka \\ \eta_l(ka) &\simeq 0 \quad ; \quad \text{for } l > ka. \end{aligned} \quad (5.13)$$

And then we can estimate

$$\begin{aligned} \sum_l^\infty (2l+1)\eta_l(ka) &\simeq - \int_0^{ka} (2l+1)\eta_l(ka) dl \\ &\quad + \text{correction terms} \\ &= -\frac{2}{9}(ka)^3 - \frac{\pi}{4}(ka)^2 + \text{lower terms} \end{aligned} \quad (5.14)$$

for large l . Such simplification is based on the assumption that a is large enough to allow us to use Debye approximation and yet small enough to allow us to neglect terms with $\sin \tau \neq 1$ in Eq. (5.11). In the negligible lower terms are included the correction terms for the summation such as arising from the removal of the terms $k=0$, Euler-Maclaurin terms, and care for the upper limit of summation, that are important to the surface energy of the plane and the spherical surface.

Since the summation with respect to m can be replaced by the approximate integration of Eq. (5.14) with respect to k over $0 \sim k_F$, we obtain

$$\Delta E_p \simeq \frac{4}{45\pi} k_F^5 a^3 + \frac{1}{8} k_F^4 a^2. \quad (5.15)$$

Substituting Eq. (5.14) in Eq. (5.9), we have

$$Q = \frac{4}{9\pi} k_F^3 a^3 + \frac{1}{2} k_F^2 a^2. \quad (5.16)$$

This is rewritten as

$$Q = \frac{4\pi}{3} a^3 \cdot \rho_0 + 4\pi a^2 \cdot \frac{k_F^2}{8\pi}.$$

The first term represents the volume effect that the infinite wall expels the free electron

gas into interior, and the second the surface effect.

With Eqs. (5.16), (5.7), we have the relation

$$a = a_0 - \frac{3\pi}{8k_F} = a_0 - b_\infty, \quad (5.17)$$

as expected from § 2.1 (ii).

Then ΔE_p is expressed in terms of a_0 as

$$\Delta E_p = \frac{4}{45\pi} k_F^5 a_0^3 + \frac{1}{40} k_F^4 a_0^2. \quad (5.18)$$

Adding ΔE_e , we obtain the total energy change

$$\Delta E = \Delta E_p + \Delta E_e = \frac{1}{40} k_F^4 a_0^2$$

proportional to the area $4\pi a_0^2$, and therefore the surface energy

$$\sigma = k_F^4 / 160\pi \equiv \sigma_s, \quad \therefore \beta = 1, \quad (5.19)$$

proving $\alpha = 1/8\pi$ for the internal surface of a large spherical cavity.

In this connection, we derive the Brager-Schuchowitzky surface energy on the simple assumption $a = a_0$;

$$\Delta E_p = \frac{4}{45\pi} k_F^5 a_0^3 + \frac{1}{8} k_F^4 a_0^2,$$

and then

$$\sigma = k_F^4 / 32\pi \equiv \sigma^{(1)}$$

and

$$Q' = \frac{4}{9\pi} k_F^3 a_0^3 + \frac{1}{2} k_F^2 a_0^2,$$

showing the defect common to $\sigma^{(1)}$, the excess interior density due to expelling $k_F^2/8\pi$ per unit area.

(ii) Cavity with small radius

We shall discuss the dependence of the surface energy of a spherical cavity on its radius explicitly, preparing for discussion of the vacancy. Now we have only to carry out numerical calculations of η_l , Q , and ΔE_p , instead of taking the approximate integral and Debye formulae.

For a given value of a , we first calculate η_l and express Q and then a_0 as function of ka . For convenience of comparison with the treatment of larger cavity, it is better to rewrite Q as

$$Q = \frac{4}{9\pi} k_F^3 a^3 + \frac{\gamma}{2} k_F^2 a^2, \quad (5.20)$$

and the result of numerical calculations is expressed by γ as a function of ka . The results for $k_F a = 0 \sim 10$ are approximated by

$$r \sim 1 - \frac{0.855}{k_F a}, \tag{5.21}$$

as shown in Fig. 7. The relation between a and a_0 is

$$a_0 = a \left(1 + \frac{9\pi}{8} \frac{r}{k_F a} \right)^{1/3} = a \cdot \left\{ 1 + 3r \left(\frac{b_\infty}{a} \right) \right\}^{1/3}. \tag{5.22}$$

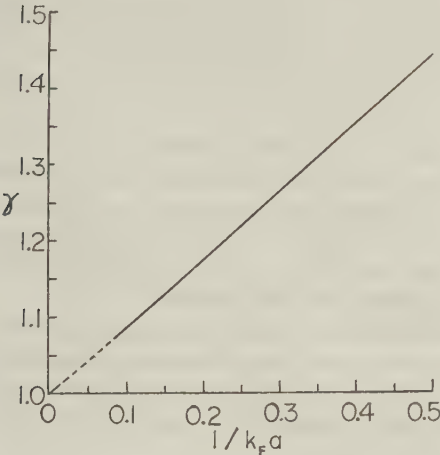


Fig. 7. γ as a function of the reciprocal of the radius a of the physical surface of the spherical cavity.

Table I. Q , $k_F a_0$, and β as function of $k_F a$.

$k_F a$	Q	$k_F a_0$	$\Delta E/\zeta$	β
0.6	0.50087	1.5241	0.10369	0.8927
0.7	0.62688	1.6425	0.12231	0.9067
0.8	0.76882	1.7581	0.14170	0.9169
0.9	0.92748	1.8716	0.16199	0.9249
1.0	1.10371	1.9833	0.18320	0.9315
1.1	1.29819	2.0936	0.20538	0.9371
1.2	1.51223	2.2028	0.22848	0.9417
1.4	2.00125	2.4185	0.27758	0.9494
1.6	2.57771	2.6314	0.33069	0.9552
1.8	3.24847	2.8423	0.38764	0.9597
2.0	4.02028	3.0516	0.44988	0.9634
2.2	4.89994	3.2597	0.51491	0.9664
2.4	5.89428	3.4667	0.58318	0.9689
2.6	7.01025	3.6730	0.65575	0.9712
2.8	8.25416	3.8785	0.73249	0.9732
3.0	9.63328	4.0835	0.81317	0.9748

The calculation of energy ΔE_p is carried out in the range $0 \leq k_F a \leq 3$, as shown in Table I. The surface energy $\sigma = \beta \sigma_s$ is obtained from the formation energy $\Delta E(Q)$ of cavity with Q ;

$$\beta(Q) = 20 \cdot (\Delta E/\zeta) \cdot (9\pi Q/4)^{-2/3} \approx 5.430 (\Delta E/\zeta) \cdot Q^{-2/3}. \tag{5.23}$$

The calculated values of β are shown in Fig. 8 and approximated by

$$\beta(k a_0) \sim 1 - \frac{0.065}{k_F a_0} - \frac{0.15}{(k_F a_0)^2}, \tag{5.24}$$

showing the continuous transition of the surface energy from the internal surface of the vacancy to the plate.

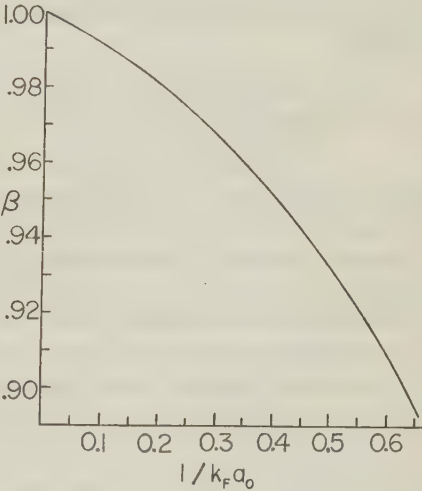


Fig. 8. β as a function of the reciprocal of the radius a_0 of the cavity.

§ 6. Application to the Formation Energy of a Vacancy

We shall now consider the dependence of β on the form of the potential barrier of cavities for fixed values of radius a_0 .

As interesting values of a_0 , we consider naturally two limiting cases; $a_0 \rightarrow \infty$ and $a_0 = r_s$. The discussion of cavity with $a_0 \rightarrow \infty$ (and yet $a_0 \ll R$) has been proved to be equal to that of the plane surface, in which the insensitiveness of β to the potential form has been proved in §§ 3, 4.

Therefore, we confine ourselves to the case $a_0 = r_s$, the atomic vacancy, to discuss the insensitiveness of β . Since $\sum_l (2l+1) \eta_l(ka)$ cannot always be expressed in a simple analytical function of ka , even if $\eta_0(ka)$ is given as a simple function of ka , we cannot discuss the problem in a general way but have to be contented with the analysis of theories of vacancy given by previous authors.

6.1 Quasi self-consistent treatment of the finite step potential

As the vacancy potential in monovalent metals, Fumi¹¹⁾ took a spherical potential barrier with radius $a=a_0=r_s$ and height $k_0^2/2$ which was adjusted so as to give $Q=1$. His model seems to be more reasonable than the infinite wall model, but requires more labour in calculations, producing approximately the same results.

Using the Born approximation in calculating η_l for $l \geq 1$, Fumi found $k_0=0.86k_F$ satisfying $Q=1$ and obtained the formation energy E_v of a vacancy

$$E_v \simeq \zeta/6,$$

which, substituted in Eq. (5.23), gives

$$\beta \simeq 0.91. \quad (6.1)$$

Seeger and Bross²³⁾ have carried out systematic calculations of E_v by using the finite step potential barrier, as Huntington took for the plane surface in § 4.1. Their results can be expressed only numerically. Four sets of their quasi self-consistent choice of (a, k_0) and the corresponding values of E_v are reproduced in Table II, supplemented by the calculated values of β . We see β for the four sets nearly equal to 0.93 for $k_0 \rightarrow \infty$.

Table II. a , ΔE , and β as function of k_0 .

$k_0 a$	$k_F a$	Q	$\Delta E_v/\zeta$	$\Delta E/\zeta$	β
∞	0.9424	1.0000	0.5715	0.1715	0.931
2.5720	1.5000	1.0000	0.5715	0.1715	0.931
1.8010*	1.9192	1.0015	0.5730	0.1724	0.935
1.5830	2.2000	1.0000	0.5834	0.1834	0.996

* Since $Q \neq 1$, corrections are made for $\Delta E/\zeta$ and β .

In the limit $k_0 \rightarrow 0$, $a \rightarrow \infty$, we can obtain, according to Fumi, the analytical expressions

$$k_F \cdot k_0^2 \cdot a^3 = 3\pi/2, \quad E_v = 4\zeta/15,$$

and then

$$\beta = \frac{16}{3} \left(\frac{4}{9\pi} \right)^{2/3} \simeq 1.448, \quad (6.2)$$

because the use of the Born approximation taken by Fumi is now justified in calculating all η_l .

β for a real vacancy potential should take a value between these two limiting values, i.e. 0.93~1.45.

6.2 Negative Hartree-Fock potential

Taking the negative Hartree-Fock potential of the free copper ion for the vacancy in copper, Seeger²⁴⁾ obtained $E_v=0.166\zeta$, from which we obtain

$$\beta = 0.90. \quad (6.3)$$

6.3 Analysis of the self-consistent potential for vacancy in copper

Huntington and Seitz⁷⁾ used the variational approach and obtained the electronic contribution to the formation energy $E_v=1.4\sim 1.9$ ev., from which we obtain

$$\beta = 1.1 \sim 1.4, \quad (6.4)$$

taking ζ for copper as 7.2 eV. in Eq. (5.23).

In addition, they found that their results are not sensitive to a form of a trial function so long as the function represents the effect of expelling just one electron.

Huntington⁸⁾, taking the exchange interaction into account self-consistently, carried out a more laborious calculation and obtained the electronic contribution $E_v=1.23$ eV., from which we have

$$\beta = 0.94. \quad (6.5)$$

A good agreement with $\beta=0.93$ for the quasi self-consistent infinite wall will be due to the same reason as in the case of the plane surface energy in § 4.3.

In order to make a more reasonable comparison, it is desirable that self-consistent calculations both of the vacancy and of the plane surface should be carried out for the same metal with the same accuracy.

6.4 Vacancy in polyvalent metals

We shall now estimate the formation energy $E_v(Z)$ of a vacancy in Z -valent metals as an extension of the previous treatment. Z -valent metals are now regarded as systems of Z free electrons per ion in the free electron model. Therefore $E_v(Z)$ is equivalent to that of the cavity with $Q=Z$ in the monovalent metal;

$$E_v(Z) = \Delta E(Z) = E_v(1) \cdot Z^{2/3} \cdot \beta(Z) / \beta(1). \quad (6.6)$$

Neglecting the small difference between $\beta(Z)$ and $\beta(1)$ and taking the approximate evaluation $E_v(1) \simeq \zeta/6$ by Fumi, we obtain

$$E_v(Z) \simeq Z^{2/3} \cdot \zeta/6. \quad (6.7)$$

As an interesting example, we apply Eq. (6.7) to the estimation of the formation energy of a vacancy in nickel. Taking $Z=0.54$, we obtain

$$E_v(0.54) \simeq 0.100\zeta \quad (6.8)$$

On the other hand the interpolated value from Table I is

$$E_v(0.54) = \Delta E(0.54) = 0.110\zeta. \quad (6.9)$$

Seeger²⁵⁾, taking the same value for Z and the quasi self-consistent infinite wall, obtained

$$E_v(0.54) = -0.074\zeta \quad (6.10)$$

by calculating $\Delta E_p = 0.326\zeta$ and $\Delta E_e = -0.4\zeta$. Evidently, E_v cannot be negative in stable lattices. He attributed this discrepancy to the disregard of the interaction with the incomplete d -electrons.

There is, however, a trivial error in his calculations; ΔE_e should be corrected so that

$$\Delta E_e = -0.4\zeta \times 0.54 = -0.216\zeta.$$

When corrected,

$$E_v(0.54) = 0.326\zeta - 0.216\zeta = 0.110\zeta \quad (6.11)$$

in a good agreement with our estimations (6.8) and (6.9).

§ 7. Surface Energy of Ellipsoidal Cavity

So far we have seen the rule $\beta \simeq 1$ for the

spherical surface. It is desirable that the rule should be confirmed for a surface with non-uniform curvature. There is an interesting example of physical significance for the check of the rule, the ellipsoidal cavity.

7.1 Formation energy of vacancy pair

A vacancy pair is a system of two vacancies arranged on the nearest neighbour lattice sites of crystals, separated by $2C$, and approximated by a cavity of rotational ellipsoid with twice the volume of the single vacancy, as shown in Fig. 9 (a), (b).

We change the variables x, y, z to ξ, η, φ by

$$\begin{aligned} x &= C \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi \\ y &= C \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi \\ z &= C \xi \cdot \eta. \end{aligned}$$

The area of the geometrical surface is given as

$$\begin{aligned} S_0(C) &= 2\pi C^2 \{ (\xi_0^2 - 1) + \sqrt{\xi_0^2 - 1} \cdot \xi_0^2 \cdot \sin^{-1}(1/\xi_0) \}, \end{aligned} \quad (7.1)$$

where ξ_0 is determined by

$$V_0(C) = \frac{4\pi}{3} C^3 (\xi_0^2 - 1) \xi_0 = \frac{4\pi}{3} r_s^3 \times 2. \quad (7.2)$$

Then the formation energy of the ellipsoidal cavity E_{v-p} is expressed as

$$E_{v-p} = \beta \sigma_s \cdot S_0(C). \quad (7.3)$$

From our rule, we expect β to be 1.0 or more closely 0.95 for the spherical cavity with $Q=2$.

Table III. β as function of the separating distance C .

$k_F C$	C/r_s	ξ_1	E_{v-p}/ζ	ξ_0	β
1.500	0.7816	1.2687	0.2805	1.8178	0.9542
1.600	0.8337	1.2298	0.2812	1.7305	0.9551
1.700	0.8858	1.1973	0.2819	1.6549	0.9559
1.800	0.9379	1.1702	0.2827	1.5891	0.9567

Seeger and Bross²³⁾ calculated E_{v-p} for the range $C/r_s = 0.78 \sim 0.94$, which includes the nearest neighbour distances in the three typical cubic structures. They solved wave eqs. on the assumption of the infinite wall on the physical surface ξ_1 , the value of which was determined by the Friedel sum rule. The results of their numerical calculation are reproduced in Table III, supplemented by the values of ξ_0 and β by Eqs. (7.2) and (7.3),

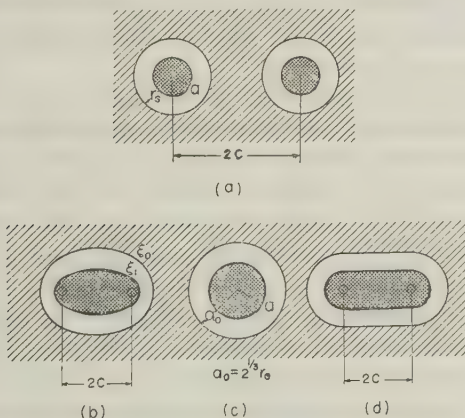


Fig. 9. Schematic illustration of the process of the transformation of the two single vacancies into one cavity, the volume of which is twice as large as the single vacancy.

(a) two single vacancies in consideration with separation distance $2C$.

(b) the vacancy pair represented by the rotational ellipsoidal cavity.

(c) the most stable cavity with the volume $Q=2$, which is equivalent to the single vacancy in divalent metals. r_e is the radius of the sphere in which one electron is found in average; $r_e \simeq r_s$ for monovalent metals and $r_e \simeq r_s Z^{-1/3}$ for Z -valent metals.

(d) another possible model for vacancy pair (cylindrical model).

respectively. The calculated values of β for all ellipsoids considered are in good agreement with our estimation 0.95.

In this model, since the association energy of a vacancy pair is difference between the formation energy of one vacancy pair and twice that of the single vacancy, it is possible to interpret the association energy simply as an energy gain due to the reduction of the total surface area when two individual spheres are transformed into one ellipsoid with the same volume.

7.2 Interaction energy between two vacancies

We can give a rough estimation of the interaction energy $E_I(C)$ between two vacancies separated by $2C$ as

$$E_I(C) \simeq 0.96\sigma_s \cdot S_0(C) - 2E_v(1) \quad (7.4)$$

by assuming $\beta=0.96$ for $C>0.94r_s$, as shown in curve 1 in Fig. 10.

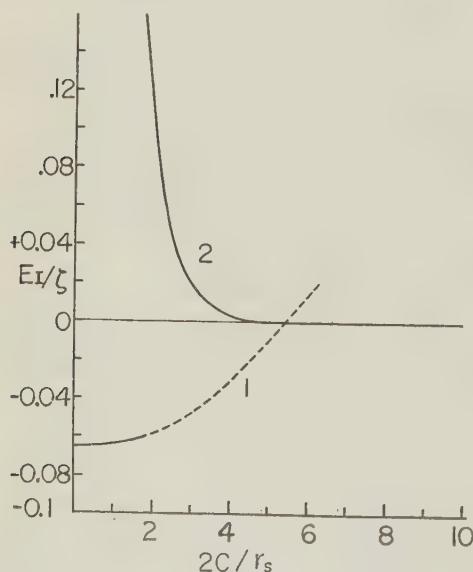


Fig. 10. Interaction energy $E_I(C)$ between two vacancies as functions of the separating distance $2C$. Curve 1 is calculated on the basis of the surface energy model, while curve 2 is based on the T-F model where the matrix metal is assumed to be silver.

Even if we assume a cylindrical cavity as shown schematically in Fig. 9(d), the interaction energy is expressed nearly analogously to curve 1 in Fig. 10, provided that β be constant over all the points on the surface regardless of the small curvature dependence.

In this model, two separated vacancies are

more stable than a vacancy pair in the range $2C>5.8r_s$. This means that the interaction is weak attraction of short range.

§ 8. Discussion and Conclusion

We have proved the approximate validity of the surface energy formula $\sigma_s=k_F^4/160\pi$ or $\beta\simeq 1$ on the basis of Friedel theorem and of the extended Weyl-Laue theorem, nearly independently of the shape and of the form of the surface potential barrier. And we have found intimate relations between the theories given independently by previous authors for the surface energy of metals, the formation energy of the vacancy and the vacancy pair, and the nuclear surface energy. Furthermore, even when our rule does not agree with some results of the previous authors^{9), 25)} we can correct their errors and find the validity of our rule.

Comparisons of the theoretical values with the experimental ones have been made by the previous authors on their particular cases, and good agreements have been obtained, although we do not reproduce numerical values of both. There is a note on the meaning of the good agreement:

(i) As for the theoretical values, σ_s is a main but only one part of the electronic contribution to the surface energy. As mentioned already, it is rather fortuitous that the negligence of the correlation and the exchange contribution is nearly compensated by the over-estimation of counting twice the interaction of electrons both in the case of plane surface and in the vacancy. There are other contributions such as distortion of surrounding ions and change in the normal modes of the vibration. The theoretical values, therefore, involve some ambiguities.

(ii) As for the experimental values, the plane surface energy is affected by the treatment and the contamination of the surface and depends on crystallographic orientations and on temperature. The vacancy energy is estimated from somewhat indirect effects. The experimental values are often found in comparatively wide range.

Therefore agreements between the experimental and the theoretical values do not necessarily prove the validity of a particular model taken as the basis of theories; for quite another model, so long as it still stands

on the free electron model, will give a good agreement.

Finally we should note a fundamental question on the free electron model with the positive jelly approximation. The free electron model for conduction electrons in periodic lattices is not justified by the similarity between the charge distribution but by that between the dependences of their energy eigen value $E(k)$ upon the wave vector k with an appropriate effective mass. Therefore we should be careful in treating the charge density, particularly when it is near the lattice points, in the free electron model.

Therefore our results are only of a first approximation. For higher approximations, we should take cell structures into account, instead of modifying the model within the positive jelly approximation.

The author wishes to express his thanks to Prof. S. Miyahara and Assist. Prof. T. Toya of Hokkaido Univ. for their advices and discussions, and to Mr. T. Inoue and Mr. M. Inagaki for their labour in numerical calculations. This work was supported in part by the research grant of the Ministry of Education.

Appendix. A criticism on T-F approach to the impurity atom in the free electron metal

Lazarus²⁶⁾, calculating the interaction energy between an impurity atom and the vacancy on the basis of the T-F relation, has succeeded in explaining the dependence of an impurity diffusion in metals on the valence difference. And then interest is refocused on the T-F approach to an impurity atom in metals²⁷⁾⁻³⁰⁾.

In these works, the formation of the vacancy is regarded as putting a "pseud" negative point charge in the uniform positive jelly.

But the T-F approach to vacancy based on the pseud point charge picture is of a poor approximation. We give two examples of failure. First it leads to negative formation energy of a vacancy, besides an infinite self-energy of the point charge. An application to the vacancy in silver gives -14.5 eV in the linearized approximation by Mott²⁷⁾, and -8.3 eV in the higher approximation by Alfred and March²⁸⁾. Secondly, it leads to repulsive interaction between two vacancies, contrary

to the tendency to form a pair. A rough estimation of the interaction in silver is made on the basis of Mott's approximation as shown in curve 2 in Fig. 10. A more accurate calculation taken recently by Alfred and March²⁹⁾ does not seem to improve the repulsive nature essentially.

Even if we replace the pseud point charge picture by a more reasonable one, for example, the spherical cavity, the T-F approach to the vacancy gives negative formation energy in the same way as seen in the derivation³⁾ of negative surface energy for the plane surface.

Accordingly, the T-F approach is not appropriate to the discussion of the vacancy energy and then the interaction energy of the vacancy-impurity complex. Therefore there is a fear in the success of Lazarus that his explanation may not be to the point.

References

- 1) N. M. March: *Advances in Phys.* **6** (1957) 1.
- 2) J. Frenkel: *Z. Phys.* **51** (1928) 232.
- 3) K. Huang and G. Wyllie: *Proc. Phys. Soc. London A*, **62** (1949) 180.
- 4) K. Huang: *Proc. Phys. Soc. London* **60** (1948) 161.
- 5) J. Bardeen: *Phys. Rev.* **49** (1936) 654.
- 6) F. J. Blatt: *Phys. Rev.* **108** (1957) 268.
- 7) H. B. Huntington and F. Seitz: *Phys. Rev.* **61** (1942) 315.
- 8) H. B. Huntington: *Phys. Rev.* **61** (1942) 325.
- 9) H. B. Huntington: *Phys. Rev.* **81** (1951) 1035.
- 10) J. Friedel: *Phil. Mag.* **43** (1952) 153; *Advances in Phys.* **3** (1954) 446; *Ann. physique* **9** (1954) 158.
- 11) F. G. Fumi: *Phil. Mag.* **46** (1955) 1007.
- 12) P. P. Eward and H. Juretschke: *Structure and Properties of Solid Surfaces* (Chicago Univ., 1953) 22; with the discussion given by C. Herring.
- 13) H. Weyl: *Math. Ann.* **71** (1911) 441.
- 14) M. v. Laue: *Ann. Physik* **44** (1914) 1197.
- 15) A. Sugiyama: *J. Phys. Soc. Japan* **14** (1959) 977.
- 16) W. J. Swiatecki: *Proc. Phys. Soc. London A*, **64** (1951) 227.
- 17) E. Feenberg: *Phys. Rev.* **60** (1941) 204.
- 18) A. Brager and A. Schuchowitzky: see ref. 4.
- 19) A. Brager: see ref. 4;
- 20) W. J. Swiatecki: *Phys. Rev.* **98** (1955) 203.
- 21) P. Debye: *Ann. Physik* **39** (1912) 789.
- 22) C. N. Watson: *Theory of Bessel Functions* (Cambridge, 1922).
- 23) A. Seeger and H. Bross: *Z. Phys.* **145** (1956) 161.

- 24) A. Seeger: *Hand. Phys.* vol. **7.1** (Springer, 1955) 403.
 25) A. Seeger: *Z. Phys.* **144** (1956) 637.
 26) D. Lazarus: *Phys. Rev.* **93** (1954) 973; *Impurities and Imperfections* (Amer. Soc. Metals, 1955) 107.
 27) N. F. Mott: *Proc. Camb. Phil. Soc.* **32** (1936) 281.
 28) L. C. R. Alfred and N. H. March: *Phys. Rev.* **103** (1956) 877.
 29) L. C. R. Alfred and N. H. March: *Phil. Mag.* **2** (1957) 985.
 30) H. Fujiwara: *J. Phys. Soc. Japan* **13** (1958) 935.
 31) H. Brooks: *Impurities and Imperfections* (Amer. Soc. Metals, 1955) 1.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Interaction of Conduction Electrons with Acoustic Waves in Simple Semiconductors

By Nobuo MIKOSHIBA

Electrotechnical Laboratory, Nagatacho, Tokyo

(Received January 9, 1960)

A semi-classical theory is given of the interaction of conduction electrons with acoustic waves in single-valley semiconductors with spherical energy surface, using Pippard's approach to the ultrasonic absorption in monovalent metals. For longitudinal acoustic waves, the acoustoelectric effect is identical with that obtained by Weinreich-Holstein's phenomenological approach, if $ql \ll 1$ and $|C| \gg m\omega_p^2/q^2 \gg 2\zeta/3$, where q is the wave number of acoustic waves, C the deformation potential constant and l, m, ω_p, ζ are the mean free path, effective mass, plasma frequency, Fermi energy (or average thermal energy) of conduction electrons respectively. Under such conditions as $ql \gg 1$ and $|C|$ and $2\zeta/3 \gg m\omega_p^2/q^2$, the acoustoelectric effect is essentially identical with that derived from the quantum-mechanical calculation. In the sufficiently low frequency range, where $ql \ll 1$ and $|C|$ and $2\zeta/3 \ll m\omega_p^2/q^2$, the interaction can be described by the term of the electronic viscosity as in monovalent metals. For transverse acoustic waves, $C=0$ in cubic crystals and the interaction is analogous to that in monovalent metals, with the two exceptions that there is no region in which the absorption coefficient depends linearly on the frequency of waves, and the coefficient approaches to the limiting value in the relatively low frequency range.

§1. Introduction

In metals, the theories^{1), 2)} of the ultrasonic absorption by conduction electrons in zero or finite magnetic field have been shown to be in good agreement with experiments.^{3), 4)} Although there is no experiment of the acoustoelectric effect in metals, reasonable theories have been recently given by Blount⁵⁾ and the present author.⁶⁾ In general, we may conclude that the interaction of conduction electrons with acoustic waves has become considerably clear in metals at present.

In contrast to metals, there are some ambiguities about the interaction in semiconductors. For example, we consider the acoustoelectric effect in semiconductors, which has been discussed so far from the various points of view. Parmenter's two approaches^{7), 8)} in the low and high frequency ranges have been shown to be deficient by several authors.⁹⁾ Weinreich-Holstein's phenomenological method^{10), 11)} led to too small effect in relatively low frequency range, at least in metals.⁶⁾ But for transverse waves in many-valley semiconductors, this

method led to the formula¹²⁾ in excellent agreement with the experiments. Therefore, it will be necessary to check the condition for the applicability of their method, using more detailed theory of the electron-acoustic wave interaction.

In relatively high frequency range, Van den Beukel's method¹³⁾ may be a reasonable approach, which is based on the treatment of the interaction as a collision problem between conduction electrons and acoustic phonon beams. In fact, the effect in metals obtained by semi-classical Boltzmann theory⁶⁾ was essentially identical with Van den Beukel's in the relevant frequency range. As has been pointed out in a previous paper,⁶⁾ the effect of the space charge in the semi-classical theory is involved implicitly in the electron-phonon coupling constant in Van den Beukel's method. In semiconductors, however, the corresponding coupling constant is due to the deformation potential, which has the different origin from the effect of the space charge. Then, it will be also necessary to check the condition for the applicability to semiconductors of Van den Beukel's method, taking the effect of the Coulomb force into account explicitly.

Roughly speaking, there are three different types in semiconductors¹⁴⁾: single-valley semiconductor with spherical energy surface such as *n*-InSb (hereafter called simple semiconductor), simple many-valley semiconductor such as *n*-Ge and degenerate single-valley semiconductor such as *p*-Ge. We restrict ourselves to the discussion of simple semiconductors in this paper. The case of many-

valley semiconductors will be discussed in the forthcoming paper.

In § 2, we shall give the basic equations for a degenerate electron gas and calculate *n* (local fluctuation of the number density of electrons), *E* (internal electric field) and *J* (internal current density), making use of Pipard's approach¹⁾ to the ultrasonic absorption in monovalent metals. In § 3, we take a typical sample of *n*-InSb to make the numerical estimations of the physical quantities involved in the basic equations. In § 4, the absorption coefficient of acoustic waves and the acoustoelectric effect are calculated for various frequency ranges. The required modifications for a non-degenerate electron gas are made in § 5. In the last section, § 6, we shall compare the obtained results with those in monovalent metals. In particular, the applicability conditions of Weinreich-Holstein's and Van den Beukel's methods are discussed in detail.

§ 2. Basic Equations

Throughout this paper, the following assumptions are made. (1) We consider only the case of one carrier. Then, of course, we ignore the recombination of electrons with holes. (2) The following two effects caused by acoustic waves are neglected: (a) ionization of electrons from impurities and (b) recombination of electrons with charged impurities.

It is necessary, for the determinations of *n*, *E* and *J*, to solve Maxwell's equation, the equation of continuity and the Boltzmann equation. Maxwell's equation is written as

$$\frac{\partial}{\partial t} \left(\mathbf{J} - Ne\mathbf{u} + \frac{\varepsilon}{4\pi} \cdot \frac{\partial \mathbf{E}}{\partial t} \right) = -\frac{c^2}{4\pi} \text{curl} \cdot \text{curl} \mathbf{E}, \quad (2.1)$$

where *N* is the number density of ionized impurities (and then equal to the density of conduction electrons in equilibrium), *u* the local velocity of impurities and *ε*, *e*, *c* are the dielectric constant, the charge of an electron, the light velocity respectively. For longitudinal waves propagating in *z*-direction, we get

$$E_z = i \frac{\omega_p^2 m}{\omega e} \left(\frac{J_z}{Ne} - u_z \right), \quad E_x = E_y = 0, \quad (2.2)$$

where $\omega_p = (4\pi Ne^2/m\varepsilon)^{1/2}$ is the plasma frequency of conduction electrons, *m* the effective mass of electrons, ω the angular frequency of acoustic waves. For transverse waves propagating in *z*-direction and polarized in *x*-direction,

$$E_x = -\frac{mk_0^2}{q^2 e \tau} \left(\frac{J_x}{Ne} - u_x \right), \quad E_y = E_z = 0, \quad (2.3)$$

where $k_0^2 = 4\pi N e^2 \omega \tau / mc^2$, τ is the relaxation time of electrons, q the wave number of acoustic waves. We neglected the displacement current in (2.3).

Next, solving the equation of continuity,

$$\frac{\partial}{\partial t}(ne) + \operatorname{div} \mathbf{J} = 0, \quad (2.4)$$

we obtain

$$n = qJ_z / \omega e \quad \text{and} \quad n = 0 \quad (2.5)$$

for longitudinal and transverse waves, respectively. The Boltzmann equation of the distribution function f is given by

$$\frac{\partial f}{\partial t} + (\mathbf{v} \cdot \nabla_r) f + \frac{e}{m} (\mathbf{E}' \cdot \nabla_v) f = - \frac{f - f_0(|\mathbf{v} - \mathbf{u}|)}{\tau}. \quad (2.6)$$

Here $\mathbf{v}$ is the velocity of electrons and

$$E_z' = E_z - i \frac{Cq^2}{\omega e} u_z, \quad E_x' = E_x. \quad (2.7)$$

C is the deformation potential constant and is the characteristic force constant in semiconductors. (For transverse waves $C=0$ in cubic crystals.) In fact, only the electric field was taken into account in Pippard's theory of monovalent metals. For mathematical simplicity, we take a degenerate electron gas model in this section. The modification needed for the Maxwell distribution will be discussed in §5. The distribution function is as follows:

$$\left. \begin{aligned} f &= f_0(|\mathbf{v} - \mathbf{u}|) - \Psi(\mathbf{v}) \cdot \partial f_0 / \partial \mathbf{v}, \\ f_0(\mathbf{v}) &= \left\{ \exp \left[\frac{1}{2} m (v^2 - v_0^2) / kT \right] + 1 \right\}^{-1}, \\ v_0 &= \frac{h}{m} \left[\frac{3}{8\pi} (N + n) \right]^{1/3}, \end{aligned} \right\} \quad (2.8)$$

where h is the Planck constant, k the Boltzmann constant, v_0 the Fermi velocity. From (2.6), (2.7) and (2.8), $\Psi(\mathbf{v})$ for longitudinal and transverse waves are given by

$$\Psi(\mathbf{v}) = \frac{aA_z}{ql} \cdot \frac{x}{1-iax} + \frac{aB}{ql} \cdot \frac{v_0}{v} \cdot \frac{1}{1-iax} - \left(u_x x + B \frac{v_0}{v} \right), \quad (2.9a)$$

$$\Psi(\mathbf{v}) = \left[\frac{aA_x}{ql} \cdot \frac{1}{1-iax} - u_x \right] \sqrt{1-x^2} \cdot \cos \phi, \quad (2.9b)$$

respectively, where we use the polar coordinates (v, θ, ϕ) about z -axis in the velocity space and put for brevity

$$x \equiv \cos \theta,$$

$$l \equiv \tau v \text{ (mean free path of electrons),}$$

$$a \equiv ql / (1 + i\omega\tau)$$

and

$$A_z \equiv \frac{eE_z'\tau}{m} + u_z, \quad A_x \equiv \frac{eE_x'\tau}{m} + u_x, \quad B \equiv nv_0/3N. \quad (2.10)$$

Using the solutions of the Boltzmann equation and the current expression

$$\mathbf{J} = \frac{2em^3}{h^3} \int_0^\infty \mathbf{v} \cdot f(\mathbf{v}) d^3v, \quad (2.11)$$

we calculate the current density as follows:

$$J_z = -\frac{3Ne\hbar}{ql} \left(\frac{A_z}{a} + iB \right) \quad (2.12a)$$

for longitudinal waves,

$$J_x = \frac{NeagA_x}{ql} \quad (2.12b)$$

for transverse waves, where Pippard's functions¹⁾

$$p \equiv 1 - (1/2) \int_{-1}^1 \frac{dx}{1 - iax}, \quad g \equiv \frac{3}{2} (1 - p - p/a^2)$$

are used. In (2.12) and hereafter, l , p , g and a mean their values at the Fermi surface.

From (2.2), (2.3), (2.5), (2.10) and (2.12), we can get the basic equations for latter uses:

(1) Longitudinal waves;

$$n = \frac{qNu_z}{\omega} \cdot Q, \quad J_z = Neu_z Q, \quad E_z = i \frac{\omega_p^2 m u_z}{\omega \epsilon} (Q - 1), \quad (2.13)$$

where

$$Q \equiv \left(1 + i \frac{\omega \tau}{(\omega_p \tau)^2} + \frac{Cq^2}{m\omega_p^2} \right) / \left(1 + \frac{aq\hbar}{3(\omega_p \tau)^2} \left(1 + i \frac{\omega \tau}{p} \right) \right). \quad (2.14)$$

Then,

$$A_z = \left(i \frac{C\tau q^2}{m\omega} u_z - u_z - i \frac{aq\hbar}{3\omega \tau} \left(1 + i \frac{\omega \tau}{p} \right) u_z \right) / \left(1 + \frac{aq\hbar}{3(\omega_p \tau)^2} \left(1 + i \frac{\omega \tau}{p} \right) \right) - i \frac{C\tau q^2}{m\omega} u_z + u_z, \quad (2.15)$$

$$B = \frac{1}{3} \cdot \frac{q\hbar}{\omega \tau} \cdot u_z Q. \quad (2.16)$$

(2) Transverse waves;

$$n = 0, \quad J_x = Neu_x P, \quad E_x = \frac{mk_0^2 u_x}{eq^2 \tau} (1 - P), \quad (2.17)$$

where

$$P \equiv \frac{g'(q^2 + k_0^2)}{q^2 + g'k_0^2}. \quad (2.18)$$

Then,

$$A_x = -\frac{q^2 + k_0^2}{q^2 + g'k_0^2} u_x, \quad (2.19)$$

where we put $g' \equiv ag/ql$.

§ 3. Numerical Estimations

To make the numerical estimations of the basic quantities, we take a typical sample of n -InSb, which is a cubic crystal and has nearly spherical energy surface. The sample with $N = 10^{16} \text{ cm}^{-3}$ may be sufficiently degenerate at very low temperatures. Then, we take the following values of physical parameters:

$$\rho(\text{density}) = 5.8 \text{ g} \cdot \text{cm}^{-3}, \quad \epsilon = 16, \quad m = 0.015 m_0 \text{ (electronic mass)}, \\ V(\text{sound velocity}) = 3 \times 10^5 \text{ cm} \cdot \text{sec}^{-1}, \quad C = -7.2 \text{ eV}, \quad \tau = 5 \times 10^{-13} \text{ sec}.$$

It is convenient to consider various frequency ranges separately, the critical frequencies of which are tabulated as

$$\begin{aligned}
 \omega_1 &= 1.2 \times 10^{10} \text{ (frequency at which } ql=1), \\
 \omega_2 &= 2 \times 10^{12} \text{ (frequency at which } \omega\tau=1), \\
 \omega_3 &= 1.1 \times 10^5 \text{ (frequency at which } q^2=|k_0^2|), \\
 \omega_4 &= 3.8 \times 10^9 \text{ (frequency at which } |C|=m\omega_p^2/q^2), \\
 \omega_5 &= 1.2 \times 10^{11} \text{ (frequency at which } 2\zeta/3=m\omega_p^2/q^2),
 \end{aligned}$$

where $\zeta \equiv mv_0^2/2$ is the Fermi energy. For longitudinal waves, we consider separately four frequency ranges to give the approximate expressions for A_z and B :

$$(1) \quad ql \ll 1, |C| \text{ and } 2\zeta/3 \ll m\omega_p^2/q^2;$$

$$A_z \cong \frac{aq_l}{3p} \left(1 - i \frac{p}{\omega\tau}\right) u_z, \quad B \cong \frac{1}{3} \cdot \frac{q_l}{\omega\tau} \cdot u_z. \quad (3.1)$$

$$(2) \quad ql \ll 1, |C| \gg m\omega_p^2/q^2 \gg 2\zeta/3;$$

$$A_z \cong \frac{aq_l}{3p} \left(1 - i \frac{p}{\omega\tau}\right) \left(\frac{Cq^2}{m\omega_p^2}\right) u_z, \quad B \cong \frac{1}{3} \cdot \frac{q_l}{\omega\tau} \left(\frac{Cq^2}{m\omega_p^2}\right) u_z. \quad (3.2)$$

$$(3) \quad ql \gg 1, |C| \gg m\omega_p^2/q^2 \gg 2\zeta/3;$$

The expressions for A_z and B are identical with (3.2).

$$(4) \quad ql \gg 1, |C| \text{ and } 2\zeta/3 \gg m\omega_p^2/q^2;$$

$$A_z \cong -\frac{i}{3} \cdot \frac{(ql)^2}{\omega\tau} \cdot \left(\frac{3C}{2\zeta}\right) u_z, \quad B \cong \frac{1}{3} \cdot \frac{q_l}{\omega\tau} \cdot \frac{q_l}{a} \left(1 - i \frac{\omega\tau}{p}\right) \left(\frac{3C}{2\zeta}\right) u_z. \quad (3.3)$$

In the above expressions, we assume that a can be taken to be real up to $\omega\tau \sim 1$, as in Pipard's theory¹⁾ in monovalent metals.

For transverse waves, we can take the following three ranges:

$$(1) \quad ql \ll 1, q^2 \ll |k_0^2|;$$

$$A_x \cong u_x/g'. \quad (3.4)$$

$$(2) \quad ql \ll 1, q^2 \gg |k_0^2|;$$

$$A_x \cong u_x. \quad (3.5)$$

$$(3) \quad ql \gg 1, q^2 \gg |k_0^2|;$$

The expression for A_x is identical with (3.5).

§ 4. Ultrasonic Absorption and Acoustoelectric Effect

We shall calculate the ultrasonic absorption and the acoustoelectric effect. For a degenerate electron gas in semiconductors, the formulae⁶⁾ for monovalent metals can be used. The absorption coefficient A and the acousto-electromotive force F are given by

$$A = \frac{3mN}{4\pi\rho V|u|^2\tau} \int_{-1}^1 dx \int_0^{2\pi} d\phi |\Psi(v_0)|^2, \quad (4.1)$$

$$F = \frac{3m\gamma}{4\pi\rho e V^2|u|^2\tau} \int_{-1}^1 dx \int_0^{2\pi} d\phi |\Psi(v_0)|^2 \quad (4.2)$$

respectively,* between which Weinreich's relation¹⁵⁾,

$$A/F = NeV/\gamma, \quad (4.3)$$

* The formula (4.2) is clearly connected with the component of the second order current of u_x or u_z , i.e. $J_1 = n_1 e v_1$, where n_1 and $v_1 \propto u_x$ or u_z . There exists another component $J_2 = N_0 e v_2$, where v_2 is the second order drift velocity. Since $v_2 \propto$ (internal force acting on electrons), J_2 has no observable dc part under zero external dc electric field. In this respect, see also references (5) and (7).

holds. Here, $\gamma \equiv \rho |u|^2 V/2$ is the acoustic energy flow density.

Substituting (2.9a), (2.9b), (3.1)–(3.5) into (4.1) and (4.2), we obtain the results for various frequency ranges as follows:

[1] Longitudinal waves:

(1) $ql \ll 1, |C|$ and $2\zeta/3 \ll m\omega_p^2/q^2$;

$$A \cong \frac{4}{15} \cdot \frac{Nm v_0^2 \tau \omega^2}{\rho V^3}, \tag{4.4a}$$

$$F \cong \frac{4}{15} \cdot \frac{m v_0^2 \tau \omega^2}{\rho e V^4} \cdot \gamma. \tag{4.4b}$$

(2) $ql \ll 1, |C| \gg m\omega_p^2/q^2 \gg 2\zeta/3$;

$$A \cong \left(\frac{Cq^2}{m\omega_p^2}\right)^2 \frac{Nm}{\rho V \tau}, \tag{4.5a}$$

$$F \cong \left(\frac{Cq^2}{m\omega_p^2}\right)^2 \frac{m}{\rho e V^2 \tau} \cdot \gamma. \tag{4.5b}$$

(3) $ql \gg 1, |C| \gg m\omega_p^2/q^2 \gg 2\zeta/3$;

$$A \cong \left(\frac{Cq^2}{m\omega_p^2}\right)^2 \frac{\pi N m v_0 \omega}{6 \rho V^2}, \tag{4.6a}$$

$$F \cong \left(\frac{Cq^2}{m\omega_p^2}\right)^2 \frac{\pi m v_0 \omega}{6 \rho e V^3} \cdot \gamma. \tag{4.6b}$$

(4) $ql \gg 1, |C|$ and $2\zeta/3 \gg m\omega_p^2/q^2$;

$$A \cong \left(\frac{3C}{2\zeta}\right)^2 \frac{\pi N m v_0 \omega}{6 \rho V^2}, \tag{4.7a}$$

$$F \cong \left(\frac{3C}{2\zeta}\right)^2 \frac{\pi m v_0 \omega}{6 \rho e V^3} \cdot \gamma. \tag{4.7b}$$

[2] Transverse waves:

(1) $ql \ll 1, q^2 \ll |k_0^2|$;

$$A \cong \frac{1}{5} \cdot \frac{Nm v_0^2 \tau \omega^2}{\rho V^3} \left\{ 1 - \frac{8}{35} (ql)^2 \right\}, \tag{4.8a}$$

$$F \cong \frac{1}{5} \cdot \frac{m v_0^2 \tau \omega^2 \gamma}{\rho e V^4} \left\{ 1 - \frac{8}{35} (ql)^2 \right\}. \tag{4.8b}$$

(2) $ql \ll 1, q^2 \gg |k_0^2|$;

$$A \cong \frac{1}{5} \cdot \frac{Nm v_0^2 \tau \omega^2}{\rho V^3} \left\{ 1 - \frac{3}{7} (ql)^2 \right\}, \tag{4.9a}$$

$$F \cong \frac{1}{5} \cdot \frac{m v_0^2 \tau \omega^2 \gamma}{\rho e V^4} \left\{ 1 - \frac{3}{7} (ql)^2 \right\}, \tag{4.9b}$$

(3) $ql \gg 1, q^2 \gg |k_0^2|$;

$$A \cong Nm/\rho V \tau, \tag{4.10a}$$

$$F \cong m\gamma/\rho e V^2 \tau. \tag{4.10b}$$

§ 5. Maxwell Distribution

We have treated hitherto a degenerate electron gas model. Some modifications needed for the Maxwell distribution will be discussed in this section. First, instead of (2.8) we must put

$$\left. \begin{aligned} f_0(v) &= \exp \left[\frac{1}{2} m (v_0^2 - v^2) / kT \right], \\ v_0^2 &= \left(\frac{2kT}{m} \right) \ln \left\{ 2^{1/2} \pi^{3/2} \left(\frac{\hbar^2}{mkT} \right)^{3/2} (N+n) \right\}. \end{aligned} \right\} \tag{5.1}$$

Then, instead of v_0 involved in $\Psi(v)$ in (2.9a) we must use

$$v_1 \equiv (3kT/m)^{1/2}. \tag{5.2}$$

Although there exist some mathematical complications for the analytical solution, it can be easily seen that the modifications are simply given by the displacement,

$$v_0^2 \rightarrow \alpha kT/m \tag{5.3}$$

in the equations below (2.12). Here α is a numerical factor of order unity depending on (1) the kinds of waves, (2) the frequency ranges, (3) the velocity-dependence of the relaxation time. Since all the essential features can be made clear in a degenerate electron gas model, we don't perform the detailed calculation of α in this paper.

§ 6. Discussions

[1] Longitudinal waves:

(1) Weinreich-Holstein's method for the low frequency range ($ql \ll 1$). We consider the case of one carrier, to which Weinreich-Holstein's method is applied. Instead of (2.12a) we put

$$J_z = -\frac{De}{kT} (N+n) \frac{\partial U}{\partial z} - De \frac{\partial n}{\partial z}, \tag{6.1}$$

where D is the diffusion constant and

$$U = U_a + U_b. \tag{6.2}$$

Here U_a is the electrostatic potential due to the charge fluctuation of electrons and is determined by

$$\partial^2 U_a / \partial z^2 = -4\pi e^2 n / \epsilon. \tag{6.3}$$

U_b is the deformation potential and is given by

$$U_b = -C u_z / V. \tag{6.4}$$

Then, we can calculate the dc current from (6.1)–(6.4) and the equation of continuity, (2.4). The accusto-electromotive force F can be derived from dividing the dc current by the electrical conductivity $\sigma \equiv Ne^2 \tau / m$. The result obtained is just identical with (4.5b). As has been pointed out by Parmenter,⁷⁾ Weinreich-Holstein's method ignores the effects of the charge of impurities and its motion induced by waves. This is the reason why

the condition $|C| \gg m\omega_p^2/q^2$ must be required, which is the same condition pointed out by Bardeen-Shockley¹⁶⁾ for the neglect of the electrostatic potential of impurities in comparison with the deformation potential.

(2) Van den Beukel's method for $ql \gg 1$. Van den Beukel's method is based on the treatment of the interaction as a collision problem between conduction electrons and acoustic phonon beams. It takes only the deformation potential term in the interaction Hamiltonian. Therefore, his method neglects undoubtedly two effects; (a) the electrostatic potential of impurities and (b) the electrostatic potential due to the charge fluctuation of electrons.

For the neutral impurity scattering, for example, his method leads to⁹⁾

$$F = \frac{(2\pi)^{1/2} C^2 m^{1/2} \omega}{\rho e V^3 (kT)^{3/2}} \cdot \gamma \quad (6.5)$$

for the Maxwell distribution, which becomes identical with (4.7b) when we put $\alpha = 3^{2/3} \pi^{1/3} / 2$. The applicability conditions of Van den Beukel's approach may be interpreted as follows: (A) $ql \gg 1$; This is the condition for the treatment of acoustic waves as phonon beams. (B) $|C| \gg m\omega_p^2/q^2$; This is the condition for neglecting the effect of the charge of impurities. (C) $2\zeta/3 \gg m\omega_p^2/q^2$; This condition is most severe for acoustic waves used practically and can be rewritten as

$$\lambda \ll 2\pi\lambda_{TF}, \quad (6.6)$$

where λ is the acoustic wave-length and

$$\lambda_{TF} = \left(\frac{\epsilon m v_0^2}{12\pi N e^2} \right)^{1/2} \quad (6.6a)$$

is the quantum analog to the Debye length in Thomas-Fermi model. For the Maxwell distribution

$$\left. \begin{aligned} \lambda &\ll 2\pi(\alpha/3)^{1/2} \lambda_D, \\ \lambda_D &= \left(\frac{\epsilon k T}{4\pi N e^2} \right)^{1/2}, \end{aligned} \right\} \quad (6.7)$$

where λ_D is the Debye length. Here, λ_D or λ_{TF} has the physical meaning of the distance within which the charge fluctuation of electrons does not vary appreciably in the magnitude. Then, (6.6) or (6.7) is interpreted as the condition under which the effect of the charge fluctuation of electrons can be ignored in the interaction Hamiltonian.

It will be necessary to study the effect of the last condition, (C), on the ordinary con-

duction problems. The wave-length of thermal phonons coupled to thermal electrons is about the same order of magnitude as de Broglie's wave-length of thermal electrons,¹⁶⁾ $\lambda_{th} \cong h/mv$. Therefore, inserting λ_{th} into (6.6) or (6.7), the condition (C) becomes

$$\hbar\omega_p \ll \zeta \quad \text{or} \quad \hbar\omega_p \ll kT \quad (6.8)$$

for the degenerate or non-degenerate cases, respectively. Then, at sufficiently high temperatures, the deformation potential theory of Bardeen-Shockley can be used without taking account of the effect of the space charge in conduction problems. On the other hand, at low temperatures where the condition (6.8) does not hold, the dominant scattering mechanism of conduction electrons is due to impurities.¹⁷⁾ In ordinary conduction problems, therefore, the effect of the space charge can be ignored in general.

(3) Low frequency range in which $ql \ll 1$. $|C|$ and $2\zeta/3 \ll m\omega_p^2/q^2$. As is seen from (4.4a) and (4.4b), the dominant mechanism in this range is due to the electronic viscosity as in the low frequency range ($ql \ll 1$) in monovalent metals.

[2] Transverse waves:

The reason why the dc current along the direction of propagation is generated by transverse waves will be interpreted from the classical point of view as follows. In the first order of u_x , the local current is in x -direction and also electrons move in z -direction without net current (e.g. viscosity mechanism). In the second order, however, net dc current in z -direction is generated owing to the finite relaxation time.

The differences of the formulae (4.8)–(4.10) from those in monovalent metals are as follows; (a) There is no frequency range in which the absorption coefficient A depends linearly on ω and is independent of τ . (b) Even in the intermediate frequency range ($ql \gg 1$, $\omega\tau \ll 1$), A approaches to the limiting value, (4.10a). (c) In the low frequency range, somewhat different formulae are derived according as $q^2 \geq |k_0|^2$.

In conclusion, we may expect to check the theory by the experiment of microwave phonon beams in future.

The author should express his thanks to M. Shibuya for the valuable discussions. He also is indebted to W. Sasaki for the constant encouragements.

References

- 1) For zero magnetic field, see A. B. Pippard: *Phil. Mag.* **46** (1955) 1104. M. S. Steinberg: *Phys. Rev.* **111** (1958) 425.
- 2) For finite magnetic field, see M. H. Cohen, M. J. Harrison and W. A. Harrison: to be published.
- 3) For zero magnetic field, see W. P. Mason and H. E. Bömmel: *J. Acoust. Soc. Amer.* **28** (1955) 930.
- 4) For finite magnetic field, see R. W. Morse, H. V. Bohm and J. D. Gavenda: *Phys. Rev.* **109** (1958) 1394. R. W. Morse and J. D. Gavenda: *Phys. Rev. Letters* **2** (1959) 250. D. H. Reneker: *Phys. Rev.* **115** (1959) 303.
- 5) E. I. Blount: *Phys. Rev.* **114** (1959) 418.
- 6) N. Mikoshiba: *J. Phys. Soc. Japan* **14** (1959) 1691.
- 7) R. H. Parmenter: *Phys. Rev.* **113** (1959) 102.
- 8) R. H. Parmenter: *Phys. Rev.* **89** (1953) 990.
- 9) For example, see the references (5), (6) and N. Mikoshiba: *J. Phys. Soc. Japan* **14** (1959) 22.
- 10) G. Weinreich: *Phys. Rev.* **104** (1956) 321.
- 11) T. Holstein: Westinghouse Research Memo 60-94698-3-M15 (1956).
- 12) G. Weinreich, T. M. Sanders and H.G. White: *Phys. Rev.* **114** (1959) 33.
- 13) A. Van den Beukel: *Appl. Sci. Research B*, **5** (1956) 459.
- 14) C. Herring: *Bell Syst. Tech. J.* **34** (1955) 237.
- 15) G. Weinreich: *Phys. Rev.* **107** (1957) 317.
- 16) J. Bardeen and W. Shockley: *Phys. Rev.* **80** (1950) 72.
- 17) For example, see P. P. Debye and E. M. Conwell: *Phys. Rev.* **93** (1954) 693.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Electrical Properties of Germanium Selenide GeSe*

By Sizuo ASANABE

Research Laboratory, Nippon Electric Co. Ltd., Kawasaki, Japan

and Atuyosi OKAZAKI

*Department of Physics, Faculty of Science, Kyusyu University,
Fukuoka, Japan*

(Received January 28, 1960)

Experimental studies were made of electrical resistivity and Hall coefficient of stoichiometric, non-stoichiometric and impurity-doped GeSe crystals over the temperature range from 100°K to 800°K. The energy gap was estimated to be nearly 1.0 eV from the slope of the resistivity curves at high temperatures. There were two ways in which hole mobility varied with temperature: one was as $T^{-2.0}$ and the other as $T^{4.3}$. The results on low temperature Hall coefficient were qualitatively interpreted on the assumption that there were two kinds of impurity levels in GeSe, one of which was acceptor level due to the impurity atoms common to all specimens and the other donor level or trapping center of holes due to germanium atoms in excess of stoichiometry. An anomalous behavior found in the Hall coefficient was explained by the same assumption as in the case of SnSe that new acceptors were introduced into GeSe by heat-treatment at high temperatures and that these introduced acceptors were annihilated by the heat-treatment at lower temperatures.

§ 1. Introduction

The systematic investigations have recently been made of IV-VI intermetallic compounds

* This work was performed at Kyusyu University.

in our laboratory with respect to the electrical properties and crystal structures. Among these compounds SnTe⁽¹⁾ and GeTe^(2), 3) were found to show so-called semi-metallic properties while SnSe⁽⁴⁾ some ordinary semi-conduct-

ing properties. The crystal structure of GeSe has been reported to be orthorhombic⁵⁾, and in connection with the same crystal structure as that of SnSe⁶⁾, it seems interesting to study the electrical properties of GeSe. An anomalous hump was found to occur at about 500°C in the Hall coefficient of quenched or non-stoichiometric specimen. In some of the intermetallic compounds e.g. InAs⁷⁾, GaAs^{8),9)} or PbTe¹⁰⁾, Hall anomalies have been reported but there seems to be no possible explanation for those anomalies. We have already found the Hall anomalies^{11),12)} in SnSe and GeSe crystals, and in the case of SnSe we have attempted to interpret the experimental results qualitatively in terms of acceptor formation by the heat-treatment at high temperatures. The validity of similar explanation is expected in the case of GeSe from its close resemblance to SnSe. In order to get the confirmation it seems essential to investigate if an increase in carrier density is caused by other mechanism than thermal generation, if the linear relationship holds between Hall voltage and magnetic field and if the Hall coefficient is affected by heat-treatment.

§ 2. Experimental Procedures

GeSe crystals were prepared as follows: germanium (a few Ω cm) and selenium (99.997%) were sealed in an evacuated silica tube or put into a graphite crucible as illustrated in Fig. 1. The silica tube or graphite crucible was further sealed into an evacuated silica tube to protect the specimen from oxidation by air caused by break-up of the silica tube on solidification. Putting the tube vertically into a furnace whose temperature was automatically controlled, it was kept at

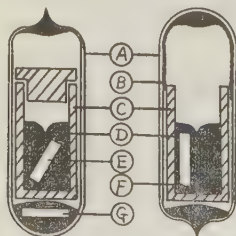
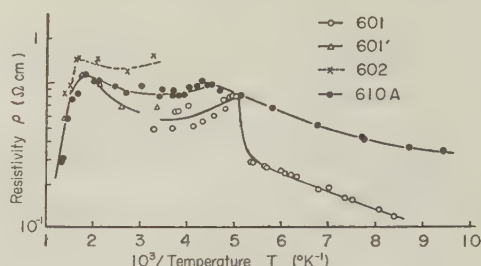
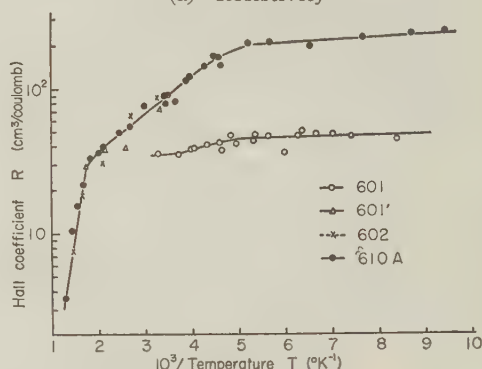


Fig. 1. Schematic indication of GeSe crystals prepared in graphite crucibles. A: silica tube, B: carbon film, C: graphite crucible, D: GeSe ingot, E: specimen 603, F: specimen 606, G: specimen 604.

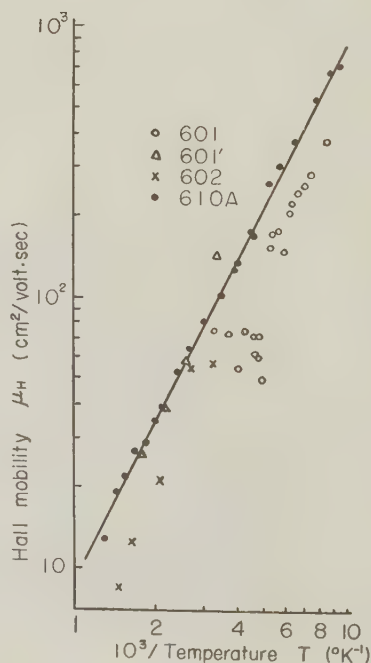
1000°C for 50 hours to get complete reaction. It was then cooled rapidly to 800°C and then with the cooling rate of 10°C per hour to



(a) Resistivity



(b) Hall coefficient



(c) Hall mobility

Fig. 2. Resistivity (a), Hall coefficient (b) and Hall mobility (c) versus inverse absolute temperature for GeSe single crystals (*p*-type) with stoichiometric compositions.

600°C (melting point of GeSe=780°C). The tube was annealed at 600°C for 12 hours and cooled to room temperature in 50 hours. Some of the specimens were prepared by quenching the tube to room temperature after the melt of germanium and selenium was violently shaken on a Bunsen burner for a few minutes. Specimens were cut in the shape of a rectangular parallelepiped whose surfaces were polished by emery-paper. An ordinary d.c. method was used on measuring the resistivity and Hall coefficient. An apparatus was the same as described in §3 of reference 11. When the resistivity of the specimen was very high at low temperatures, a microammeter and a vacuum tube voltmeter were used in place of a potentiometer.

§ 3. Experimental Results

(i) Resistivity and hall coefficient

The electrical resistivity ρ and Hall coefficient R have been measured over the temperature range from 100°K to 800°K. The d.c. current and magnetic field were applied

parallel and perpendicular, respectively, to the plane perpendicular to c-axis of the single crystal. A family of resistivity or Hall curves indicates that there should be four groups of crystals into which the resistivities or Hall coefficients are classified: they are single crystals, polycrystals with stoichiometric compositions, non-stoichiometric crystals and impurity-doped crystals.

In Fig. 2 (a), (b) and (c) are, respectively, shown the values of ρ , R and Hall mobility $\mu_H (=R/\rho)$ for GeSe single crystals. Figs. 3, 4 and 5 show the similar experimental results on polycrystalline, non-stoichiometric and impurity-doped GeSe, respectively. The specimens used in these investigations are listed in Table I. The ingots from which the specimens 603, 604 and 605 were cut were prepared in graphite crucibles as illustrated in Fig. 1. The ascending straight lines with increasing temperatures in the mobility curves of Figs. 3 (c), 4 (c) and 5 (c) were drawn proportional to $T^{4.3}$ and descending straight lines in those of Figs. 2 (c), 3 (c) and 4 (c) to $T^{-2.0}$.

Table I. Description of specimens.

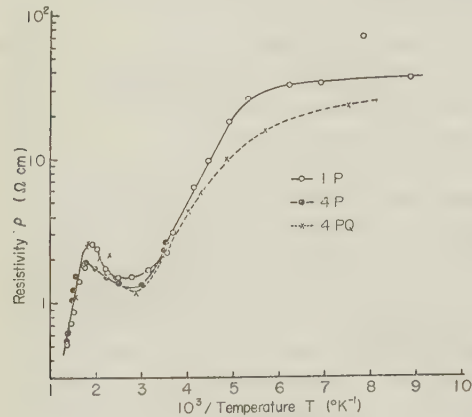
Specimens	Origins of component materials		Original compositions	Crystal growth rate	Crystal type
	Ge	Se			
601	E.P.	D.	GeSe	slow cooling	single
601'	E.P.	D.	GeSe	slow cooling	single
602	E.P.	D.	GeSe	slow cooling	single
610 A	E.P.	S.K.	GeSe	slow cooling	single
1 P	E.P.	S.K.	GeSe	slow cooling	poly
4 P	E.P.	S.K.	GeSe	slow cooling	poly
4PQ		4 P	4 P	quenching	poly
603	E.P.	D.	GeSe	slow cooling	poly
604	E.P.	D.	GeSe	slow cooling	poly
606	E.P.	A.S.	GeSe	slow cooling	poly
608Q	E.P.	A.S.	GeSe	quenching	poly
609 Q	E.P.	A.S.	GeSe _{0.95}	quenching	poly
609 A		609 Q	609 Q	slow cooling	poly
2IP		1P	1P+1%I	slow cooling	poly
3IPQ		unknown	GeSe+5%I	quenching	poly
4BIP		4P	4P+1%Bi	slow cooling	poly
4SBP		4P	4P+1%Sb	slow cooling	poly
4SBA		4SBP	4SBP	slow cooling	poly

Symbols: E.P. Eagle Picher Co.
D. Dengen-Sya.
S.K. Shindengen Kogyo K.K.
A.S. American Smelting and Refining Co.

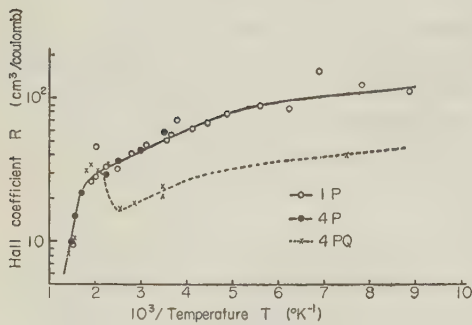
(ii) *Field dependence of ρ or R*

In connection with the Hall anomaly, it seems essential to study if there holds a linear

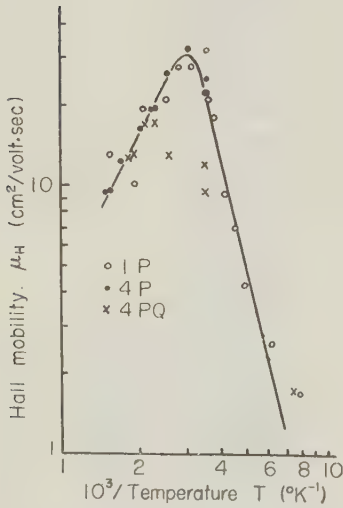
relationship at room temperature between applied electric field and current or if the Hall voltage is proportional to magnetic field at the temperature corresponding to the Hall anomaly. In Fig. 6, the potential drop V between the resistivity probes is plotted against the electric current I at room temperature for the specimen 4PQ which exhibits the Hall anomaly. Fig. 7 shows the relationship between the Hall voltage V_H and magnetic field H for the same specimen over the tempera-



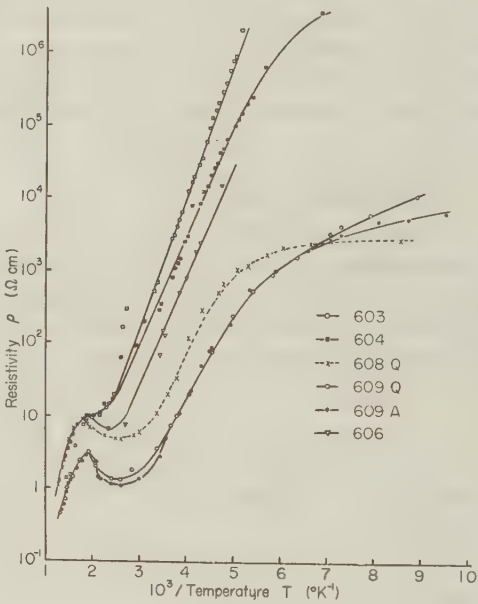
(a) Resistivity



(b) Hall coefficient



(c) Hall mobility



(a) Resistivity



(b) Hall coefficient

Fig. 3. Resistivity (a), Hall coefficient (b) and Hall mobility (c) versus inverse absolute temperature for GeSe polycrystals (*p*-type) with stoichiometric compositions.

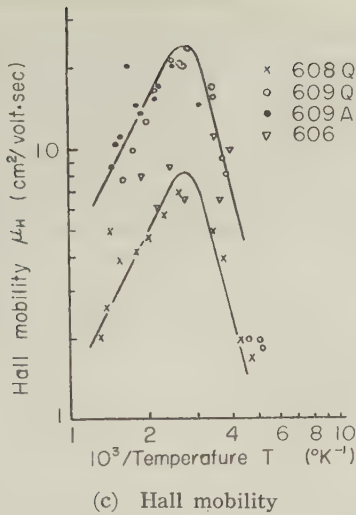


Fig. 4. Resistivity (a), Hall coefficient (b) and Hall mobility (c) versus inverse absolute temperature for GeSe crystals (*p*-type) with non-stoichiometric compositions.

ture range from 16°C to 285°C where the Hall anomaly is observed.

(iii) *Hall anomaly versus heat-treatment*

It was seen that a large Hall anomaly was observed at about 500°K in the quenched

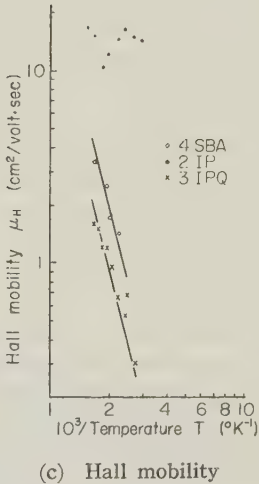
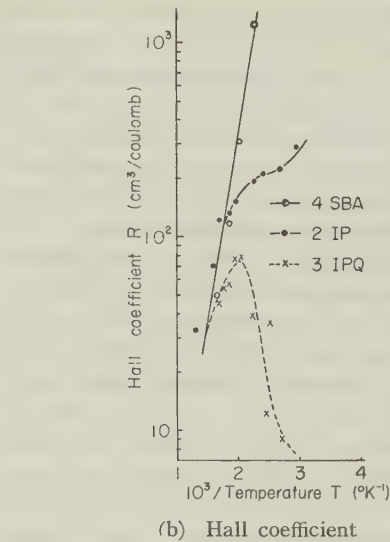
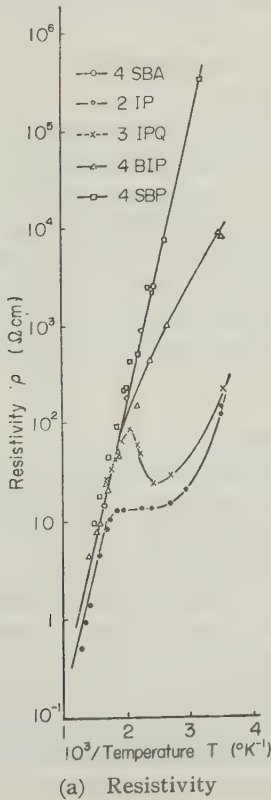


Fig. 5. Resistivity (a), Hall coefficient (b) and Hall mobility (c) versus inverse absolute temperature for impurity-doped GeSe crystals (*p*-type).

specimens. Here, we studied if the Hall anomaly might be interpreted in terms of acceptor generation by heat-treatment at high temperatures and annihilation of induced acceptors by heat-treatment at lower temperatures, as it was probably the case in SnSe. Firstly, the investigations were carried out to study how ρ and R depended on the temperature and time of the heat-treatment. The specimen sealed in an evacuated Pyrex tube was suddenly put into a furnace whose temperature was kept at 200°C, 310°C and 530°C, respectively. It was kept, respectively, at 200°C for 15 hours and at 310°C and 530°C

for 15 minutes, and then quenched to room temperature by taking it out of the furnace. Then ρ and R were measured at room temperature. The results are shown in Table II where the calculated hole concentrations, the temperature and the time of the heat-treatment are included for three different specimens. Throughout the heat-treatment, calculated Hall mobility remains nearly constant. Fig. 8 shows the typical aspect of the acceptor formation by heat-treatment at 440°C and its annihilation by heat-treatment at 220°C.

Secondly, we studied how the temperature dependence of ρ or R was affected by quenching or annealing of the specimen 4PQ. This specimen exhibited the Hall anomaly as grown. The values of ρ , R and μ_H are shown in Fig. 9. The considerable changes in ρ or R were

Table II. Changes in hole concentrations at room temperature with heat-treatment in vacuum.

Heat-treatment		Hole concentrations (cm ⁻³)		
Temp.	Period	610A	609Q	1P
530°C	15 mins.	7.67×10^{17}	4.77×10^{17}	1.08×10^{18}
310°C	15 mins.	4.98×10^{17}	2.50×10^{17}	2.00×10^{17}
200°C	15 hrs.	1.42×10^{17}	1.24×10^{17}	1.32×10^{17}

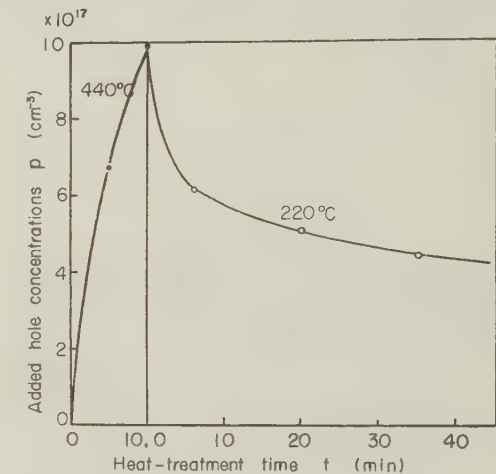


Fig. 8. A typical variation of added hole concentrations with heat-treatment time at 440°C and 220°C for GeSe single crystal 610A.

caused by the heat-treatment but there were little changes in μ_H .

(iv) Photoconductive properties

If GeSe was irradiated with 10 W white light lamp, a few tenth meter apart from the specimen, the resistivity decreased by a considerable amount. The fractional changes in the resistivity were, for instance, 20% for the specimen 603, 4% for 4P at room temperature and 50% for 604 at 150°K, respectively.

§ 4. Discussion

(i) Resistivity and hall coefficient

While four specimens 603, 604, 606 and 608Q were originally in stoichiometric compositions as seen in Table I, the resistivity and Hall curves were found to belong to rather non-stoichiometric group. This is interpreted as follows: when the stoichiometric amounts of germanium and selenium are melted and solidified in a graphite crucible sealed into an evacuated silica tube as illustrated in Fig. 1, it is expected that the ingot inside the crucible

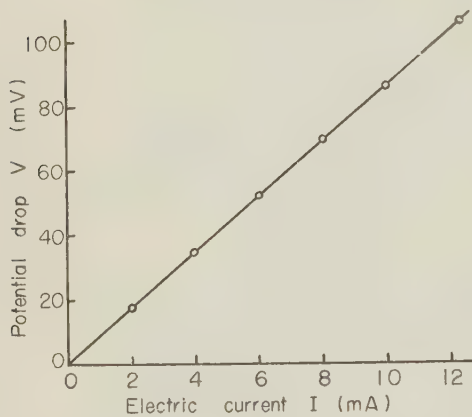


Fig. 6. Linear relation between potential drop and electric current at room temperature for quenched GeSe crystal 4PQ showing Hall anomaly.

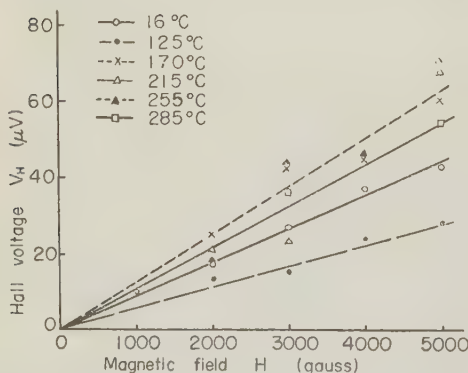
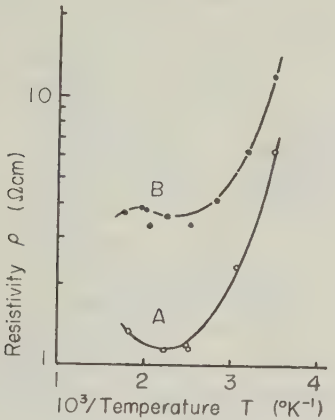


Fig. 7. Linear relationship between Hall voltage and magnetic field at various temperatures for quenched GeSe crystal 4PQ showing Hall anomaly.

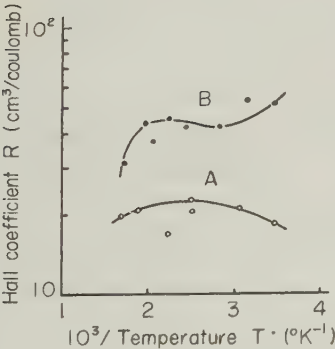
contains more germanium atoms and ingot outside the crucible more selenium atoms in deviation from stoichiometry. In reality, the crystal outside the crucible has yellow-green color which is characteristic to $\text{GeSe}_{2.13}$ crystal. The specimen 608Q is considered to be germanium-rich because it has experienced

such a short period of melting that the complete reaction of germanium with selenium was not expected.

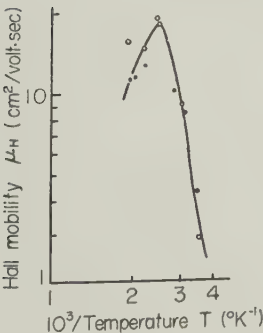
From Figs. 2 (b), 3 (b) and 4 (b) it is seen that the Hall coefficients of stoichiometric specimens decrease slowly with increasing temperature and fall abruptly at about 500°K . The non-stoichiometric specimens have larger values of the Hall coefficient at low temperatures but nearly the same values at about 500°K compared with those in stoichiometric specimens. All of the specimens in Fig. 3 (b) and the specimen 4PQ in Fig. 2 (b) exhibit the Hall anomaly which will be discussed later. Neglecting the Hall anomaly, we can interpret the Hall data qualitatively just as in the case of gold-doped germanium¹⁴⁾. We assume two kinds of impurity levels in GeSe: one is an ordinary acceptor level ($N_a\text{cm}^{-3}$) originating from impurities whose concentration is equal in all specimens and whose ionization energy is very small. Another is a donor level ($N_d\text{cm}^{-3}$) which originates from germanium atoms in excess of stoichiometry and located below a half of the energy gap between the conduction band and the valence band in the energy band diagram. According to Kröger's proposition¹⁵⁾, germanium atoms located in interstitials or vacancies of GeSe lattice may act as donors because germanium is more electropositive than selenium. The proposed energy band diagram in GeSe is shown schematically in Fig. 10. Figs. 10 (a) and 10 (c) show, respectively, the specimen



(a) Resistivity



(b) Hall coefficient



(c) Hall mobility

Fig. 9. Resistivity (a), Hall coefficient (b) and Hall mobility (c) versus inverse absolute temperature for $\text{GeSe}_{0.95}$ crystal 609Q. Curves A and B were obtained on quenched and annealed crystals, respectively.

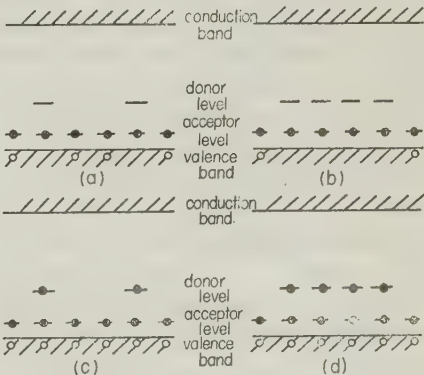


Fig. 10. Schematic diagram of proposed energy diagram in GeSe crystals. (a): with small N_a at low temperatures. (b): with large N_a at low temperatures. (c): with small N_a at higher temperatures. (d): with large N_a at higher temperatures.

with small N_a at low and high temperatures, and Figs. 10(b) and 10(d) one with large N_a at low and high temperatures, respectively. In low temperatures the concentration of free holes decreases with increasing N_a as shown in Figs. 10(a) and 10(b). It is reasonable that the Hall coefficients of non-stoichiometric specimens in which N_a is considered to be large are larger than those of stoichiometric specimens as seen in Figs. 2(b), 3(b) and 4(b). As the donor is located below a half of the forbidden band it plays effectively a role of an acceptor at high temperatures. Because of this the concentration of holes in exhaustion range equals to N_a , being independent of N_a as illustrated in Figs. 10(c) and 10(d). This is in good agreement with the experimental results that the Hall coefficients of specimens both with stoichiometric and with non-stoichiometric compositions are nearly equal in exhaustion range as seen in Figs. 2(b), 3(b) and 4(b). The temperature dependence of Fermi level is greatly affected by the value of N_a relative to N_a and this results in the diversity of the slope of the Hall curves in low temperature range: the slope equals to zero when $N_a=0$ and then increases with increasing N_a . It may be concluded from Figs. 2(b), 3(b) and 4(b) that N_a is nearly zero for the specimen 601 and increases from 1P to 608Q via 610A and 609Q. If N_a is greater than N_a the ionization energy of the donor can be estimated from the slope of the curve of $\ln R$ versus $1/T$ in low temperatures. The value of about 0.2 eV is obtained in Hall curves of the specimens 608Q and 606. In impurity-doped specimens both iodine and antimony atoms seem to act as donors and the antimony-doped specimen shows nearly intrinsic properties even at room temperature. This is reasonable if there is any covalent character in GeSe and iodine atoms or antimony atoms enter into the lattice by substitution for germanium atoms.

Remarkable differences from sample to sample in the resistivity curves were observed below room temperature. The values of the resistivity in low temperature range are small for stoichiometric single crystals but large for stoichiometric polycrystals and further larger for non-stoichiometric crystals. The resistivities of three specimens prepared in the graphite crucibles are especially large and do not

saturate in low temperatures. At high temperatures the resistivities can be approximated by a straight line common to all specimens. Though acceptor generation occurs at high temperatures as will be described later, we can estimate an energy separation between conduction band and valence band by assuming that a formation energy of an acceptor is small compared with half of the energy gap in GeSe. The value of about 1.0 eV was obtained as the energy gap by assuming that ρ was proportional to $\exp(-E_g/2kT)$.

It is sometimes more convenient to discuss about the mobility than about the resistivity if the information as to the temperature dependence of carrier concentrations is obtained from the Hall measurements. The mobility of holes in stoichiometric single crystals varies as $T^{-2.0}$ as seen in Fig. 2(c). While the hole mobility of polycrystals both with stoichiometric and with non-stoichiometric compositions varies as $T^{-2.0}$ above 350°K, but below that temperature it decreases with decreasing temperature as $T^{4.3}$ as illustrated in Figs. 3(c) and 4(c). In the case of impurity-doped specimens except 2IP the hole mobility varies as $T^{4.3}$ from room temperature up to the highest temperature investigated. $T^{-2.0}$ dependence of the mobility is explained on the assumption of both optical and acoustical mode scatterings. On the contrary, $T^{4.3}$ dependence is not clear but the scattering by the grain boundaries is considered to play an important role, probably.

(ii) Hall anomaly

The anomalous phenomenon that the Hall coefficient increases with increasing temperature before the onset of intrinsic conduction cannot be explained by an elementary semiconductor model. If the carrier is created by some other mechanism than thermal generation or if the Hall voltage is not proportional to magnetic field, then the anomalous hump of the Hall coefficient may be expected to occur. If the application of an electric field may produce an avalanche excitation of carriers¹⁶⁾ below the temperature corresponding to the Hall anomaly, the increase in carrier concentrations would then cause a sharp drop in the Hall coefficient at that temperature. From Fig. 6 it is seen that Ohm's law holds in the current-voltage range used in the experiment at room temperature and no possi-

lity of avalanche may be expected.

The Hall coefficient is usually derived by V_H/IH neglecting the higher terms than H^3 , where V_H , I and H are, respectively Hall voltage, electric current and magnetic field. If H^3 term were too large to be neglected at the temperature where the Hall anomaly occurs, the value derived by V_H/IH would show a larger value than true value of the Hall coefficient. In Fig. 6 we see that the Hall voltage is proportional to magnetic field at temperature corresponding to the Hall anomaly. The attempt to explain the Hall anomaly in terms of nonlinearity between V_H and H is also denied.

There is an other mechanism for the explanation of the Hall maximum: two holes model in Ge¹⁷⁾ or mixed conduction of electrons and holes in SnTe¹⁸⁾. In the case of Ge or SnTe the phenomena involved are reversible with temperature, but it is not the case for SnSe or GeSe. As seen in Table II or Fig. 8 the concentrations of holes increase by the high temperature heat-treatment and decrease by the low temperature heat-treatment. This situation is similar to one in SnSe reported in the previous paper. Though the investigation was not so completely made as in SnSe, the Hall anomaly may be explained by assuming that an acceptor with small ionization energy is generated by high temperature heat-treatment and annihilated by low temperature heat-treatment. The above assumption was made on SnSe and may be valid in the case of GeSe considering the fact that both SnSe and GeSe belong to IV-VI compounds and have same crystal structure and *p*-type semiconducting properties. As seen in Figs. 2(b), 3(b) and 4(b) the Hall anomaly is observed to be remarkable in non-stoichiometric specimens though they were prepared by same slow cooling as in stoichiometric specimens. This suggests that acceptor generation is enhanced by the presence of the lattice imperfections which might be caused by the deviation from the stoichiometry. In order to make clear the validity of the assumption that the Hall anomaly is attributed to acceptor generation and annihilation

by heat-treatment, it is desired that the perfection of the crystal is controlled artificially and the study is made on the relation between the densities of dislocation and the induced acceptors.

The authors should express their sincere thanks to Dr. T. Okada, Messrs. Y. Matsuoka and K. Hashimoto for their interests in the present investigation. One of us (S.A.) is greatly indebted to Dr. Y. Ishikawa, chief of the fundamental research section, for his continued encouragement.

References

- 1) K. Hashimoto and K. Hirakawa: J. Phys. Soc. Japan **11** (1956) 716.
- 2) Y. Moriguchi and Y. Koga: J. Phys. Soc. Japan **12** (1957) 100.
- 3) S. Asanabe and A. Okazaki: Mem. Fac. Sci. Kyusyu Univ. Ser. **B**, **2** (1958) 136.
- 4) Y. Matsukura, T. Yamamoto and A. Okazaki: Mem. Fac. Sci. Kyusyu Univ. Ser. **B**, **1** (1953) 98.
- 5) A. Okazaki: J. Phys. Soc. Japan **13** (1958) 1151.
- 6) A. Okazaki and I. Ueda: J. Phys. Soc. Japan **11** (1956) 470.
- 7) O. G. Folberth and H. Weiss: Z. Naturforsch. **11a** (1956) 510.
- 8) O. G. Folberth and H. Weiss: Z. Naturforsch. **10a** (1955) 615.
- 9) J. T. Edmond, R. F. Broom and F. A. Cunneil: *Report of the Meeting on Semiconductors* (held by the Physical Society, London 1956) 109.
- 10) K. Shogenji and S. Uchiyama: J. Phys. Soc. Japan **12** (1957) 252.
- 11) S. Asanabe: J. Phys. Soc. Japan **14** (1959) 281.
- 12) S. Asanabe and A. Okazaki: Proc. Phys. Soc. London **73** (1959) 824.
- 13) S. Asanabe and A. Okazaki: to be published.
- 14) W. C. Dunlap, Jr.: Phys. Rev. **97** (1955) 614.
- 15) F. A. Kröger: J. Phys. Chem. Solids **7** (1958) 277.
- 16) G. Dresselhaus, A. F. Kip and C. Kittel: Phys. Rev. **92** (1953) 827.
- 17) T. Fukuroi and K. Hanzawa: reported at the Meeting of the Physical Society of Japan, Oct. 31, 1956.
- 18) T. Okada and A. Nishiyama: reported at the Meeting of the Physical Society of Japan, Oct. 30, 1956.

Low Field Magnetoresistance Effect of Plastically Deformed n-type Silicon

By Koji KAMADA

*Sony Corporation, Shinagawa, Tokyo, Japan**

(Received February 2, 1960)

Magnetoresistance, Hall effect and resistivity are measured for n-type silicon which has been plastically deformed by compression, and it is found that the symmetry relation between relaxation time tensor and effective mass tensor is violated, although it holds in *as grown* silicon sample. It is ascribed to the presence of dislocation scattering, violating the original symmetry of relaxation time tensor of lattice scattering. Read's theory is extended, when magnetic field is parallel to dislocation line, to explain the magnetoresistance in the presence of dislocation on the basis of spherical energy surface, and dislocation density, radius of space charge cylinder around the dislocation, and fraction of dislocation sites that have accepted electrons are estimated.

§ 1. Introduction

For several years it has been known¹⁾ that plastic deformation of n-type germanium causes a pronounced reduction both in carrier density and mobility. In p-type germanium, on the other hand, plastic deformation has negligible effect on the transport properties. It is therefore believed that dislocations act as acceptor sites in germanium.

Read²⁾ has considered the nature of dislocations in germanium, taking into account the fact that they act as acceptors. In n-type germanium the acceptor sites along the dislocation are partially filled and the dislocation line is negatively charged. The charge is neutralized by a cylindrical space charge of fixed donors around the dislocation. Read ascribes the mobility effects to these space charge tubes which may occupy an appreciable fraction of the total volume of the deformed material. In silicon, however, few of the experimental works have been published concerning the effects of dislocation on the transport properties.

Magnetoresistance experiments on single crystal silicon were carried out by Pearson and Herring³⁾. In their experiment samples were cut with their length along [100], [110] and [111] directions. Based upon the nearly vanishing longitudinal magnetoresistance along the [100] direction, they suggested that the energy surfaces consisted of six ellipsoids

along the [100] axes corresponding to six minima along these directions somewhere between the center and the edge of the Brillouin zone.

Herring and Vogt⁴⁾ have noted if the relaxation time is a tensor which is diagonal in the same coordinate system as the effective mass (a situation which exists if the carriers are scattered by transverse acoustic phonons^{5,6)}, or by impurities⁷⁾), the magnetoresistance analysis yields the ratio of the effective masses, divided by the ratio of longitudinal to transverse relaxation times.

We have measured the magnetoresistance, Hall effect and resistivity of n-type silicon which has been plastically deformed by compression, and found the violation of the symmetry relation between relaxation time tensor and effective mass tensor, which holds in our *as grown* silicon sample. We have ascribed it to the presence of dislocation scattering, violating the original symmetry of relaxation time tensor of lattice scattering. We have extended Read's theory²⁾, magnetic field is parallel to dislocation line, to explain the magnetoresistance in the presence of dislocation on the basis of spherical energy surface, and estimated dislocation density, radius of space charge cylinder around dislocation and fraction of dislocation sites that have accepted electrons.

§ 2. Experimental Procedures

Three rods measuring about 4mm × 6mm × 16mm were obtained from adjacent regions

* Now at Japan Atomic Energy Research Institute, Tokai, Ibaragi, Japan.

of phosphorus-doped single crystal grown by pulling method in the [111] direction. The rods were oriented as shown in Fig. 1-a by light-figure method within the error of $\pm i^0$. One of the rods was compressed along [021] direction in Ar atmosphere at about 960°C, another was just heated in the same atmosphere and

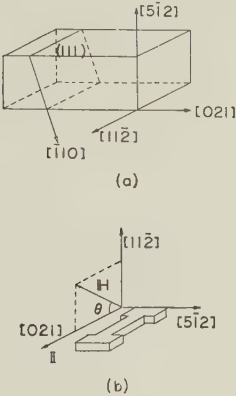


Fig. 1-a, -b. Orientation of a rod to be compressed (a) and a bridge for measurement of magnetoresistance (b). Direction of compression is along [021] direction, and dislocation line on primary slip plane is along $[11\bar{2}]$ direction.

at the same temperature for the same time interval as the compressed one, but not compressed. It was a sample to test the effect of heat treatment. The last one was kept *as grown*. Bridge-shaped samples were cut from the above three rods. Photo. 1 and Fig. 1-b show the illustrations of the bridges and its orientations respectively. As-doped gold plate electrodes were attached by locally heating the bridges. It was ascertained that this process did not affect the measured electrical behaviors of the samples. The apparatus used to make the measurements was conventional, consisting of a Dewar, a sample holder, calibrated Pt-PtRh thermocouple mounted on the sample holder, and an electromagnet. The magnetic field was determined from the magnet field current by means of a calibration against a standard magnet using germanium Hall effect piece. Runs were made by cooling the apparatus with liquid nitrogen. Measurements, both for Hall effect and magnetoresistance, were made with both polarities of magnetic field. The currents through the samples were measured by D.C. milliammeter. All voltages were measured by potentiometer-

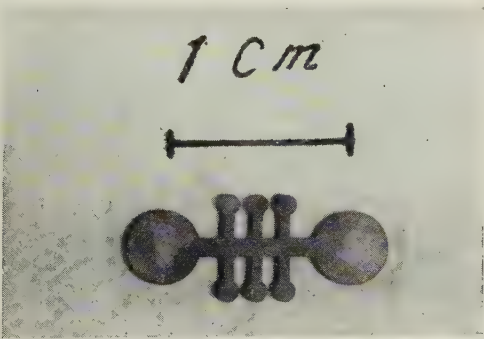


Photo. 1. Photograph of oriented silicon bridge for measuring magneto-resistance.

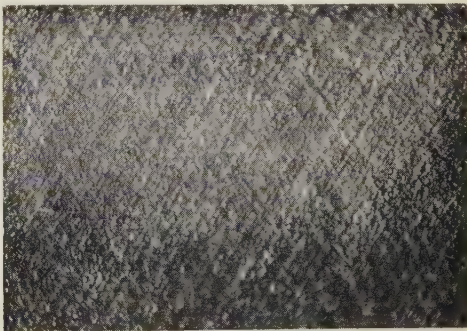


Photo. 2. Photograph of double-slipped sample after etching to reveal dislocation.

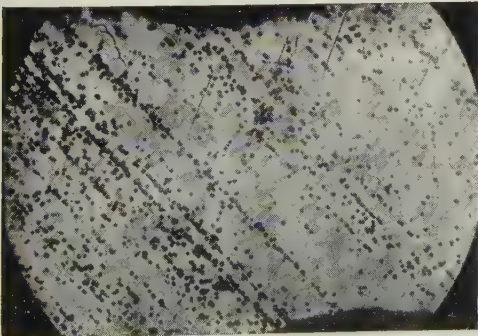


Photo. 3. Photograph of single-slipped sample after etching. Dislocation density $N=2.3 \times 10^4/\text{cm}^2$.

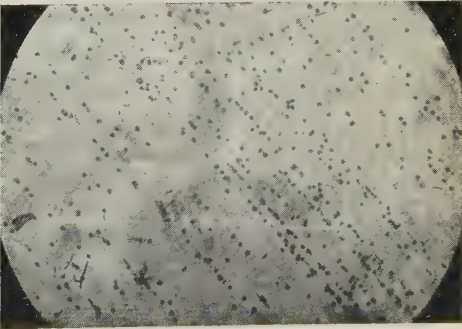


Photo. 4. Photograph of single-slipped after etching. $N=1.7 \times 10^4/\text{cm}^2$.

galvanometer system. Geometries of the bridges were measured by micrometer. Besides the above mentioned samples, we also worked with two other samples obtained from another ingot with the same doping material, phosphorus, and the same resistivities as afore-mentioned sample. The only difference was the amount of compression, i.e., these samples were compressed lighter than before, resulting in single slips over an appreciable area of the rods. Photo. 3 and Photo. 4 show the photographs of the samples after etching to reveal dislocation pits.

§ 3. Experimental Results

A) Magnetoresistance vs. field strength.

Measurements were first made of $\rho - \rho_0/\rho_0 H^2 = \Delta\rho/\rho_0 H^2$ as a function of magnetic field. Directions of current, **I**, and magnetic field, **H**, with respect to the crystal axes are shown in Fig. 1-b. θ is the angle between **I** and **H**. Since current is always along the length of

bridges, the direction of current is fixed in any given sample and is along [021] axis. The results, $\Delta\rho/\rho_0 H^2$ vs. H , are given in Fig. 2 and Fig. 3 for *as grown* and double-slipped samples respectively. The results for heat treated sample were coincident with *as grown* sample within experimental error, although they are not given in the above figures. We have not performed this experiment for single-slipped samples. In order to calculate certain fundamental constants to be described in later section it is necessary to determine $\Delta\rho/\rho_0 H^2$ as H approaches zero for various directions of **H**. These data are also shown in the above figures. The general features of these curves are:

1) The magnitudes of magnetoresistance are considerably reduced for double-slipped sample as compared with *as grown* sample. This is because of the reduction of mobility by the presence of dislocations.

2) In *as grown* sample experimental values for $\theta=90^\circ$ are larger than for $\theta=0^\circ$, although the converse is true for double-slipped sample.

3) Curves for double-slipped sample are horizontal up to 6000 Gauss indicating an exact square law relationship between $\Delta\rho/\rho_0$ and H . Curves for *as grown* sample, on the other hand, do not flatten even at low fields. These may be because of the reduction of relaxation time for the former and $\epsilon\tau/mc$ becoming much smaller than that of the *as grown* sample.

B) Magnetoresistance vs. angle θ .

Measurements were next made of $\Delta\rho/\rho_0 H^2$ for fixed values of magnetic field strength and temperature and a fixed direction of current, i.e., [021] direction, but with varying direction of magnetic field with respect to the crystal axes. Magnetic field was set at either 4600 Gauss or 5200 Gauss. Fig. 4 gives the results of such measurements on *as grown* sample, two kinds of single-slipped samples which are shown in Photo. 3 and Photo 4 and on a double-slipped sample. For the single-slipped samples magnetic field was set at 5200 Gauss, and solid circles indicate the results for the one of $N=1.7 \times 10^{14}/\text{cm}^2$ and open circles are for the one of $N=2.3 \times 10^{14}/\text{cm}^2$. Because the experimental value at a fixed angle is the average of two polarities of magnetic field as mentioned before, two values with 180° separation on a curve are equal.

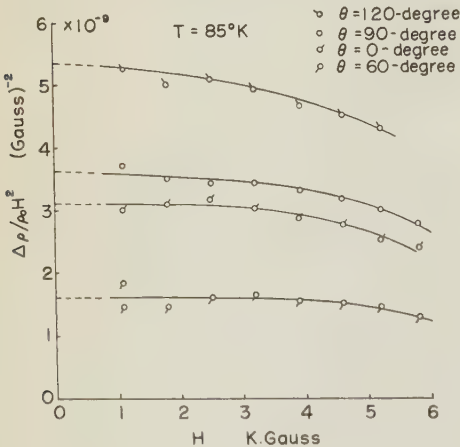


Fig. 2. $\Delta\rho/\rho_0 H^2$ vs. magnetic field for *as grown* sample.

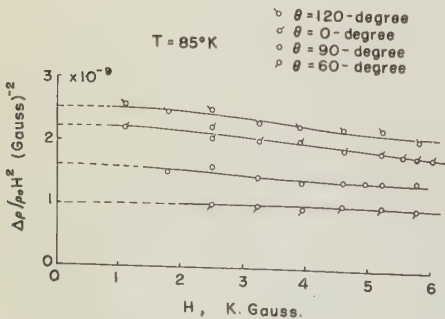


Fig. 3. $\Delta\rho/\rho_0 H^2$ vs. magnetic field for double-slipped sample.

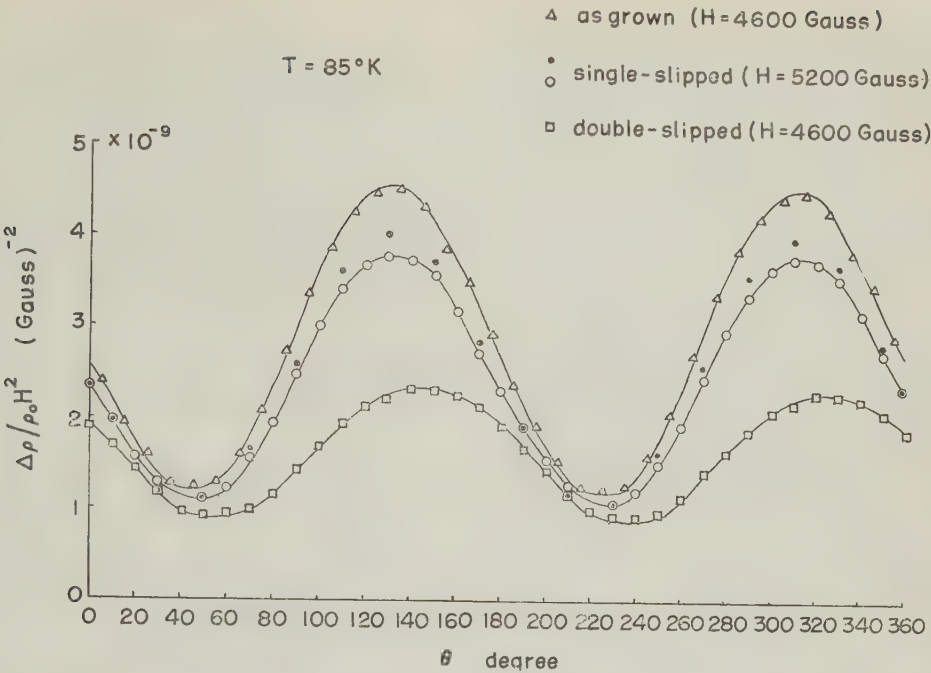


Fig. 4. Magnetoresistance vs. the angle between **I** and **H**. **I** is along [021] direction and **H** rotates in the plane which is made of [021] and $[11\bar{2}]$ axes.

The occurrence of maximum and minimum points near 50° and 130° respectively in *as grown* sample are the consequence of large departure of crystal axes of our samples from cubic axes of the crystal. It shall be shown later from the phenomenological theory of Seitz⁸⁾.

§ 4. Discussion

After the phenomenological theory of Seitz⁸⁾, the magnetoresistance in the system shown in Fig. 1-b is given as follows.

$$M = \frac{\Delta\rho}{\rho_0 H^2} = b + \frac{4d}{15} + (c + \frac{31d}{75}) \cos^2 \theta + \frac{6d \sin 2\theta}{5\sqrt{30}}, \tag{1}$$

b , c and d are constants introduced by Pearson and Suhl⁹⁾, and are given

$$\begin{aligned} b &= -(\beta + \rho_0 \alpha^2) \rho_0 \\ c &= -(\gamma - \rho_0 \alpha^2) \rho_0 \\ d &= -\delta \rho_0, \end{aligned}$$

where α , β , γ and δ were given in Seitz's theory as functions of effective mass and relaxation time, and ρ_0 is specific resistivity in the case of no magnetic field.

Table I. Limiting values of $\Delta\rho/\rho_0 H^2$ as H approaches zero.

	M_0 $\times 10^9$	M_{60} $\times 10^9$	M_{90} $\times 10^9$	M_{120} $\times 10^9$
as grown	3.1	1.6	3.6	5.35
double-slipped	2.2	1.0	1.6	2.5

The limiting values of $\Delta\rho/\rho_0 H^2$ as H approaches zero are given in Table I for $\theta = 0^\circ, 60^\circ, 90^\circ$ and 120° for both *as grown* and double-

Table II. Constants b , c , d and $b+c+d$ calculated from Table I and Eq. (I).

	$\theta = 0, 60, 90\text{-degree}$				$\theta = 90, 120, 0\text{-degree}$			
	$b \times 10^9$	$c \times 10^9$	$d \times 10^9$	$(b+c+d) \times 10^9$	$b \times 10^9$	$c \times 10^9$	$d \times 10^9$	$(b+c+d) \times 10^9$
as grown	6.23	3.58	-9.88	-0.07	6.23	3.58	-9.88	-0.07
double-slipped	2.65	2.23	-3.95	0.93	2.65	2.23	-3.95	0.93

slipped samples. These values are obtained from Fig. 2 and Fig. 3. The constants b, c and d are calculated from Table I using Eq. (1), and are given in Table II with values of $(b+c+d)$. There are given in Table II two values for each constant, one of them is calculated from M_0, M_{60} and M_{90} , and the other is from M_{90}, M_{120} and M_0 . Both values coincide accurately. As stated in the literature⁵⁾, $b+c+d$ is proportional to the magnetoresistance when both current and magnetic field are oriented along 100 direction, which is the direction of principal axis of energy ellipsoid in conduction band of n-type silicon. Therefore it must be zero provided the assumption of relaxation time tensor having the symmetry of the energy ellipsoids holds^{5), 10)}. In *as grown* sample this condition is fulfilled within experimental error, however it is violated in double-slipped sample. This violation increases as the amount of compression increases (Table III; The values of this table were calculated from Fig. 4 without taking the limiting values, consequently they are

Table III. Variation of constants b, c, d and $b+c+d$ with amount of the deformation.

	$b \times 10^9$	$c \times 10^9$	$d \times 10^9$	$(b+c+d) \times 10^9$
as grown	5.3	3.0	-8.4	-0.1
single-slipped	3.9	2.31	-5.7	0.51
double-slipped	2.28	1.62	-3.14	0.76

different from the values tabulated in Table II.). We ascribe these features to the result of mixing of dislocation scattering with lattice scattering. According to Read²⁾, in the coordinate system in which the dislocation line is along z -axis, relaxation time tensor of dislocation scattering is given as follows,

$$\frac{1}{\tau_D} = \begin{pmatrix} \frac{1}{\tau_1} & 0 & 0 \\ 0 & \frac{1}{\tau_1} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \tau_1 = \tau_1(v_1), \quad (2)$$

where v_1 is the velocity component in the plane perpendicular to dislocation line. We choose the coordinate system as shown in Fig. 1-b. Then in the coordinate system of the energy ellipsoids, i.e., that of cubic axes of crystal, the above matrix becomes

$$\frac{1}{\tau_D} = \frac{1}{\tau_1} \begin{pmatrix} \frac{5}{6} & -\frac{1}{6} & \frac{1}{3} \\ -\frac{1}{6} & \frac{5}{6} & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{15} \end{pmatrix}. \quad (3)$$

Total relaxation time tensor, i.e., the sum of the reciprocals of the relaxation time tensors of lattice and dislocation scatterings, is

$$\frac{1}{\tau} = \frac{1}{\tau_l} + \frac{1}{\tau_D} = \begin{pmatrix} \frac{5}{6\tau_l} + \frac{1}{\tau^{(1)}} & -\frac{1}{6\tau_l} & \frac{1}{3\tau_l} \\ -\frac{5}{6\tau_l} & \frac{5}{6\tau_l} + \frac{1}{\tau^{(2)}} & \frac{1}{3\tau_l} \\ \frac{1}{3\tau_l} & \frac{1}{3\tau_l} & \frac{1}{15\tau_l} + \frac{1}{\tau^{(3)}} \end{pmatrix}, \quad (4)$$

where the relaxation time tensor for lattice scattering in this system is

$$\frac{1}{\tau_l} = \begin{pmatrix} \frac{1}{\tau^{(1)}} & 0 & 0 \\ 0 & \frac{1}{\tau^{(2)}} & 0 \\ 0 & 0 & \frac{1}{\tau^{(3)}} \end{pmatrix}. \quad (5)$$

Therefore, the mixing of the dislocation scattering violates the symmetry relation between the relaxation time tensor and effective mass tensor, which is diagonal in the above coordinate system as $1/\tau_l$. Another influence of the dislocation on scattering mechanism may be the change of the effective mass tensor because of the presence of stress field around the dislocations although we do not discuss it here.

Table IV. Hall constants, resistivities and Hall mobilities calculated from them.

	$R \times 10^{-4}$ cm ³ /Coul	ρ Ω cm	μ_H 10^{-8} cm ² /V-sec	
as grown	1.46	1.08	13.5	$T = 85^\circ\text{K}$
double-slipped	2.25	3.64	6.17	
as grown	1.52	8.31	1.83	$T = 300^\circ\text{K}$
double-slipped	1.9	11.0	1.7	

Hall constants, resistivities and Hall mobilities are tabulated in Table IV. The formation of the acceptor centers by deformation

is evident from the data.

§ 5. Estimation of Dislocation Density and Radius of Space Charge Cylinder

Read²⁾ has calculated conductivity and Hall effect on the basis of simplified model of dislocations. We have calculated magnetoresistance in the presence of dislocation extending his results to higher order term in magnetic field when magnetic field is parallel to dislocation line, namely, $\theta=90^\circ$ in Fig. 1-b.

In the following discussions we set current flow in x-direction, and magnetic field and dislocation line both parallel to y-direction (Fig. 5).

Using experimental values of conductivities and magnetoresistances together with following theoretical results we have estimated the dislocation density and the radius of space charge cylinder around the dislocations. We have further estimated the fraction of dislocation sites that have accepted electrons from the results, and obtained good agreement with Read's analysis.

In following calculation we have assumed spherical energy surface, and ignored impurity scattering. Further, we have neglected the existence of two kinds of slip systems in our double-slipped sample. One of the slip systems is (111) $[\bar{1}10]$, and dislocation line is along $[11\bar{2}]$ which is also the direction of magnetic field in our measurement of M_{90} . But the other is (11 $\bar{1}$) and dislocation line is along $[1\bar{1}2]$ direction making about 42° with the above magnetic field.

It might be supposed that dislocation den-

sity could be measured directly by etch pit counting. But actually, dislocation density $N > 10^7/\text{cm}^2$ cannot be reliably estimated by direct counting because of the overlapping of etch pits.

Let f and f_0 be distribution function of electrons in perturbed and non-perturbed system respectively. We begin with the equation of continuity in momentum space

$$\frac{\partial f}{\partial t} = e \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H} \right) \nabla_p f. \quad (6)$$

It will be understood that all time derivative in this section refer to changes due to the fields only. We expand f in a series in powers of the magnitudes E and H , i.e.,

$$f = f_0 + f_1 + f_2 + f_3, \quad (7)$$

where

$$\left. \begin{aligned} f_1 &\propto E \\ f_2 &\propto EH \\ f_3 &\propto EH^2 \end{aligned} \right\}. \quad (8)$$

f_3 refers to the magnetoresistance term. Substituting Eq. (7) into Eq. (6) and equating the terms of same powers in E and H , we obtain

$$\frac{\partial f_1}{\partial t} = e \mathbf{E} \nabla_p f_0, \quad (9)$$

$$\frac{\partial f_2}{\partial t} = \frac{e}{c} \mathbf{v} \times \mathbf{H} \nabla_p f_1, \quad (10)$$

$$\frac{\partial f_3}{\partial t} = \frac{e}{c} \mathbf{v} \times \mathbf{H} \nabla_p f_2. \quad (11)$$

In following discussions, we shall concern only the consequences of Eq. (11), namely, magnetoresistance only. Read's theory concerns the consequences of Eq. (9) and Eq. (10). When magnetic field is parallel to dislocation line, f_2 is given as follows after Read's theory,

$$f_2 = \frac{e\omega}{kT} E_x f_0 \tau^2 v_z, \quad \omega = \frac{eH}{mc}, \quad (12)$$

where τ is

$$\frac{1}{\tau} = \frac{1}{\tau_t} + \frac{1}{\tau_1}, \quad (13)$$

τ_t and τ_1 are the relaxation times of lattice and dislocation scatterings respectively. Further, τ is given as follows (Fig. 5),

$$\tau = \frac{1}{v \left(\frac{1}{l_t} + \frac{\sin \varphi}{l_1} \right)}, \quad (14)$$

where l_t and l_1 are mean free paths of lattice and dislocation scatterings respectively. On

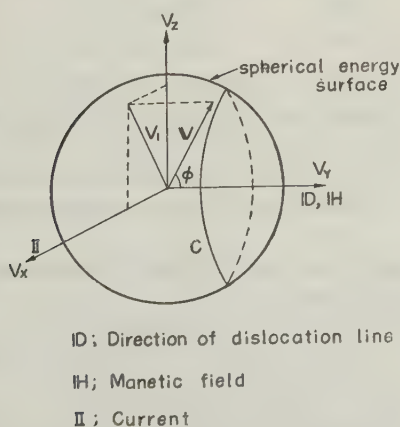


Fig. 5. Illustration of various quantities used in § 5.

substituting Eq. (12) into Eq. (11), remembering that $H=H_y$ only and $\mathbf{v} \times \mathbf{H}\nabla_p$ is the derivative in a direction tangent to the constant energy surface and in a plane normal to $\mathbf{H}$, namely on the circle c in Fig. 5, and further f_0 and τ are constant over this circle, we obtain

$$\frac{\partial f_3}{\partial t} = \frac{e^2 \omega^2}{kT} f_0 \tau^2 v_x E_x. \quad (15)$$

Eq. (15) shows that $\partial f_3 / \partial t$ due to the field is proportional to v_x . Thus the arguments²⁾ applied to f_1 also apply to f_3 and we have the following equation due to scattering

$$\dot{f}_3 = -\frac{f_3}{\tau}. \quad (16)$$

Then, in equilibrium

$$\frac{\partial f_3}{\partial t} + \dot{f}_3 = \frac{\partial f_3}{\partial t} - \frac{f_3}{\tau} = 0, \quad (17)$$

resulting to

$$f_3 = \frac{e^2 \omega^2}{kT} \tau^3 v_x E_x f_0. \quad (18)$$

The next step is to calculate additional current due to the f_3 . The current is (Fig. 5)

$$\begin{aligned} I_x^{(3)} &= e \int v_x f_3 ds \\ &= \frac{e^3 \omega^2}{kT} E_x \int v_x^2 \tau^3 dn, \end{aligned} \quad (19)$$

where s is state density and

$$dn = f_0 ds = v^2 \sin \varphi \exp\left(-\frac{mv^2}{2kT}\right) d\varphi d\vartheta dv.$$

Consequently,

$$I_x^{(3)} = \frac{e^3 \omega^2}{kT} E_x \frac{n}{2} \int_0^{\pi/2} \left(\frac{1}{l_t} + \frac{\sin \varphi}{l_1} \right)^3 d\varphi, \quad (20)$$

where n , electron density, is given by

$$\frac{n}{2} = 4\pi^{3/2} kT / 2m^2.$$

Conductivity changes due to magnetic field is given as

$$\sigma_0 - \sigma = -\frac{e^3 \omega^2}{kT} \frac{n}{2} \int_0^{\pi/2} \frac{\sin^3 \varphi}{\left(\frac{1}{l_t} + \frac{\sin \varphi}{l_1} \right)^3} d\varphi, \quad (21)$$

where σ and σ_0 are conductivities with and without magnetic field, respectively. According to Read, σ_0 is given by

$$\sigma_0 = \frac{ne^2}{kT} \langle v \rangle l_\mu F_1,$$

where

$$\frac{1}{l_\mu} = \frac{3}{l_t} + \frac{8}{\pi} \frac{1}{l_1},$$

and $\langle v \rangle$ is the thermal velocity of electron and F_1 is a numerical factor which is nearly equal to unity. Therefore the magnetoresistance M is given by

$$M = \frac{\sigma_0 - \sigma}{\sigma} = -\frac{e\omega^2}{2\langle v \rangle l_\mu F_1} \int_0^{\pi/2} \frac{\sin^3 \varphi}{\left(\frac{1}{l_t} + \frac{\sin \varphi}{l_1} \right)^3} d\varphi. \quad (22)$$

We shall discuss two cases;

1) $l_1 \rightarrow \infty$, i.e., dislocation scattering is not present. Then Eq. (22) becomes

$$M_\infty = -\frac{e\omega^2 l_t^2}{\langle v \rangle F_1}. \quad (23)$$

(2) $l_1 \sim l_t$, i.e., both lattice and dislocation scatterings are present. In this case M is given by Eq. (22).

M and M_∞ refer respectively to the magnetoresistance of deformed and *as grown* samples. The ratio of these two quantities is

$$\frac{M}{M_\infty} = \frac{1}{2} \left(3 + \frac{8}{\pi} \frac{l_t}{l_1} \right) \int_0^{\pi/2} \frac{\sin^3 \varphi}{\left(1 + \frac{l_t}{l_1} \sin \varphi \right)^3} d\varphi.$$

Fig. 6 shows Eq. (24) as a function of l_t/l_1 .

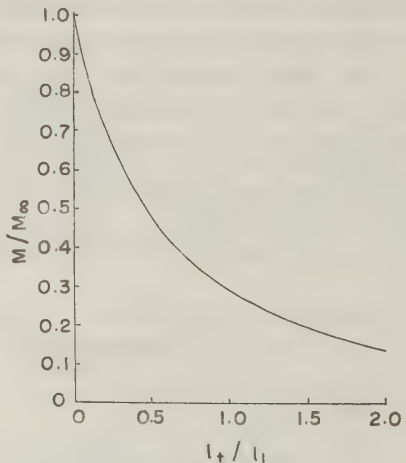


Fig. 6. Plot of Eq. (24) as a function of l_t/l_1 .

l_t , mean free path of lattice scattering, is given as follows¹¹⁾,

$$\begin{aligned} l_t &= 4.12 \times 10^{-2} \left(\frac{m_n T}{m} \right)^{1/2} \mu_H \\ &= 5.25 \times 10^{-5} \text{ cm}, \end{aligned} \quad (25)$$

where effective mass of electrons, m_n , is put equal to free electron mass, m , and μ_H is the

Hall mobility of *as grown* sample measured at 85°K (Table IV).

Consequently, we can estimate l_1 , mean free path of dislocation scattering, from measurements of M and M_∞ using Fig. 6 and Eq. (25). On the other hand, l_1 can be calculated from the density of dislocations N and the radius of space charge cylinder R_0 , namely,

$$l_1 = \frac{3}{8NR_0} \quad (26)$$

The fraction of volume occupied by the space charge cylinders, ε , is given from the definition

$$\varepsilon = \pi R_0^2 N \quad (27)$$

On the other hand, we can estimate ε experimentally by the measurement of resistivities of deformed and *as grown* samples, ρ^* and ρ respectively, using next equation and Read's plot²⁾ of $(1-\varepsilon)g(\varepsilon)$ vs. ε .

$$\rho = \rho^*(1-\varepsilon)g(\varepsilon) \quad (28)$$

Therefore, using Eq. (26) and Eq. (27) we can obtain R_0 and N .

According to the above-mentioned procedures we have estimated R_0 and N numerically. Referring to M_{90} 's of Table I, we obtain

$$\frac{M}{M_\infty} = 0.445.$$

The ratio of resistivities at 85°K is (Table IV)

$$\frac{\rho}{\rho^*} = 0.297.$$

Consequently

$$l_1 = 9.1 \times 10^{-5} \text{ cm}, \quad \varepsilon = 0.52.$$

From Eq. (26) and Eq. (27) we obtain

$$\begin{aligned} R_0 &= 4000 \text{ \AA} \\ N &= 10^8/\text{cm}^2. \end{aligned} \quad (29)$$

As it was impossible to estimate N directly, we calculated the fraction f' of dislocation sites that have accepted electrons from the above obtained numerical values of N and ε using the relation

$$\varepsilon = \frac{N/s'}{N_D - N_A} f',$$

where s' is the distance between adjacent dangling bonds and $N_D - N_A$ is the net donor density. Putting $s' = 5\text{\AA}$ and $N_D - N_A = 4.1 \times 10^{14}$, which is estimated from the measurement of Hall constant at room temperature,

we obtain

$$f' \approx 0.1.$$

Read has given the statistical theory for the filling of dislocation acceptor sites for several different models, resulting $f' = 0.087 \sim 0.099$ at 85°K. Our estimation is in good agreement with his results.

§ 6. Conclusion

Measurements of magnetoresistance of plastically deformed n-type silicon is reported. Violation of the symmetry relation between relaxation time tensor and effective mass tensor is ascertained. Theoretical consequences of Read's theory to explain the magnetoresistance in the presence of dislocation are discussed. Together with the measurements of resistivities and Hall constants, the dislocation density, the radius of space charge cylinder and the fraction of occupation of dislocation acceptor sites are estimated. The fraction of occupation of dislocation acceptor sites thus obtained is in good agreement with Read's analysis.

The present author wish to thank Mr. S. Iwata of this laboratory, Dr. Y. Uemura and Mr. E. Matsuura of Tokyo University for valuable discussions during the progress of this work. Thanks are also due to Mr. K. Hoshi of this corporation for supplying the excellent single crystal silicon ingots.

References

- 1) G. L. Pearson, W. T. Read and F. J. Morin: Phys. Rev. **93** (1954) 666.
- 2) W. T. Read: Phil. Mag. **45** (1954) 775. **45** (1954) 1119; **46** (1955) 111.
- 3) G. L. Pearson and C. Herring: Physica **20** (1954) 975.
- 4) C. Herring: Bell Syst. Tech. J. **34** (1955) 237.
- 5) C. Herring and E. Vogt: Phys. Rev. **101** (1956) 944.
- 6) W. Dumke: Phys. Rev. **101** (1956) 531.
- 7) F. Ham: Phys. Rev. **100** (1955) 1251 (A).
- 8) F. Seitz: Phys. Rev. **79** (1950) 372.
- 9) G. L. Pearson and H. Suhl: Phys. Rev. **83** (1951) 786.
- 10) R. A. Laff and H. Y. Fan: Phys. Rev. **112** (1958) 317.
- 11) W. Shockley: *Electrons and Holes in Semiconductors* (D. Van Nostrand Company Inc., 1950) 289.

Growth and Evaporation of Tungsten Oxide Crystals

By Hatsujiro HASHIMOTO, Kenzo TANAKA
and Eiji YODA

Department of Physics, Faculty of Science, Kyoto University

(Received December 26, 1959)

Growth and evaporation processes of tungsten oxide crystals formed on a surface of metallic tungsten filament at elevated temperature were observed continuously by an electron microscope. In the temperature ranges of 700~1300°C, 1300~1600°C and 1600~1800°C, needle crystals, lump-like crystals and thin films were grown up respectively, but they soon disappeared by evaporation, and above 2000°C, no crystals were grown. The effect of preliminary heating of the specimen filament in air on the crystal growth was also ascertained.

It became clear that the material needed for crystal growth was supplied from the vapour phase, and a simple relation between growth rate and needle diameter was obtained.

§ 1. Introduction

Many researches have been performed on the crystals of metallic oxide in recent ten years or so⁽¹⁾⁻⁽¹¹⁾. Arnold and Koonce⁽¹⁾ and Pfefferkorn⁽²⁾ have observed the needle type crystals grown on the surfaces of almost all elementary metals when they were heated in air and held at elevated temperatures. Takagi⁽³⁾ confirmed, independently, by electron diffraction that the needle crystals were the oxides of base metals. But any information on the process of such crystal growth was hardly obtained because of technical difficulties of continuous observations.

Many reports on the needle type crystals of tungsten oxide have been published⁽⁷⁾⁻⁽¹¹⁾. Especially Takagi⁽⁷⁾ found a condition favourable to the growth of the needle crystals and discussed the role of the oxide already existed on the base metal before heating of the specimen in vacuum. He also gave some data on the crystal structure of the needle crystal. But some ambiguities on the growth mechanism and chemical composition of the crystal were left unsolved.

In order to observe continuously the whole process of crystal growth, we have made a special specimen holder⁽¹²⁾ by which the temperature of the metallic samples can be elevated close to their melting point without giving any hurt to the apparatus, especially onto a pole piece of an objective lens. Some results obtained by this apparatus were reported previously⁽¹³⁾, in which a tungsten wire

was used as the specimen in order to grow needle crystals of tungsten oxide in vacuum of 3×10^{-3} mmHg at 850°C. It was ascertained that these crystals were the γ -tungsten oxide ($\text{WO}_{2.72}$)⁽¹⁴⁾ and the needle axis was parallel to the b -axis of the monoclinic system, and the needle had a bundle structure which consisted of parallel microcrystals with azimuths distributed around the b -axis. In this paper, the results of further research will be reported in detail.

§ 2. Experimental Procedure

For high temperature observation without any hurt to the apparatus by heat radiation it is necessary to use high efficiency furnaces with small heat capacity. Besides, easy controlling and precise adjustment of specimen temperature are desirable. From these points of view we used metallic filaments of 0.08 mm and 0.1 mm in diameter as specimens, which were heated directly by an electric current.

Fig. 1 shows the cross-section of specimen chamber of an electron microscope with three stage lenses. A specimen (1) of thin metallic filament is connected to the tips of copper terminals (2) of electric wires (3). Electron beam is introduced through a hole into the center of the specimen holder. The specimen and the terminal parts are covered by a copper cap (4) to protect the apparatus from heat radiation and from smearing by evaporated substance. To obtain specimen tem-

perature from 700°C to 3000°C by this specimen chamber, electric power of 0.6–6 watts was sufficient in the case of tungsten filament of 0.08 mm in diameter. Deflection of the image caused by magnetic field produced by heating current was so slight that it was easily adjustable.

The temperature of the specimen under observation was determined by a current-temperature diagram, which had been made previously by use of an optical pyrometer through a glass window. This diagram would be influenced by the degree of vacuum in which the sample was exposed, but in vacuum of 10^{-4} mmHg and 10^{-3} mmHg the difference of temperature was less than the error of pyrometer reading.

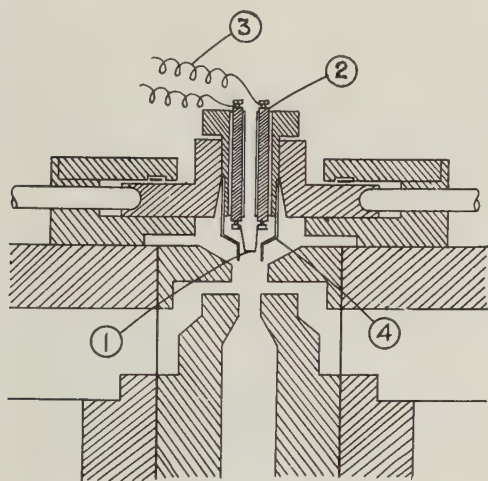


Fig. 1. Specimen heating device at high temperature.

- 1) Thin metallic filament.
- 2) Copper terminals.
- 3) Lead wire.
- 4) Copper cap.

§ 3. Observations

As reported previously⁷⁾ the growth of needle crystals of oxide is hardly observed by heating the polished tungsten filament in vacuum. In the present experiment dark grey filament was used as the sample, which had been left in air for a long time. And preliminary heat-treatment of the filament in air at 300–500°C for an hour accelerated the growth of needle crystals as compared with the case of no such treatment. Moreover, we recognized some differences in dimensions and in the mode of growth between these

two different samples.

(a) Case of no preliminary heating in air

When the tungsten filament without preliminary heating in air was heated in the specimen chamber in vacuum, many small crystals of tungsten oxide were grown up on the surface of the filament. The pressure in the specimen chamber was varied in the range from 10^{-2} to 10^{-4} mmHg. The most suitable pressure for continuous observation

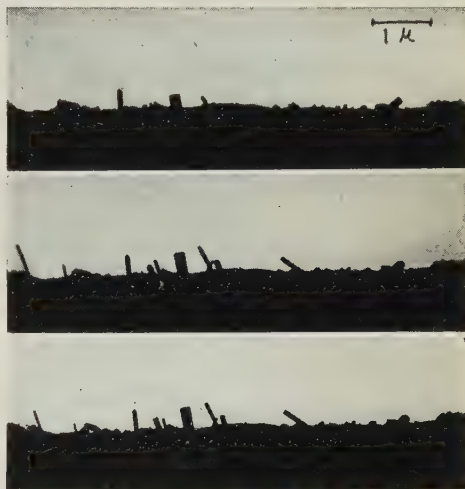


Photo. 1. Growth of needle crystals at 850°C in 3×10^{-3} mmHg on tungsten filament without preliminary heating in air.



Photo. 2. Evaporation of needle crystals at 1000–1300°C in 3×10^{-3} mmHg. 1) 5 min, 2) 15 min and 3) 20 min after beginning of heating.



Photo. 3. The lump-like crystal at 1300–1600°C.

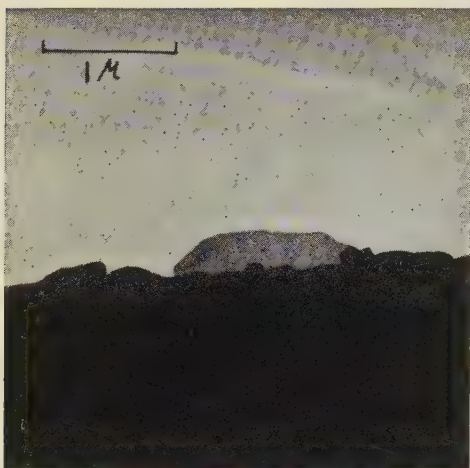


Photo. 4. Thin film of WO_3 .

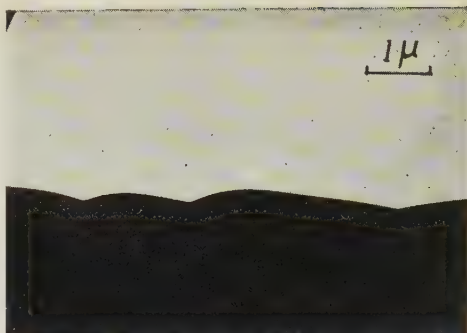


Photo. 5. Surface remained after evaporation of thin film above 2000°C .



(a) 20 min.



(b) 25 min.



(c) 30 min.



(d) 35 min.

Photo. 6. Growth of needle crystals at 900°C in $4\times 10^{-4}\text{mmHg}$ on tungsten filament with preliminary heating in air at 500°C for an hour.

was 3×10^{-3} mmHg. Photo. 1 shows the growth of the needle crystals at 850°C and in 3×10^{-3} mmHg. In this figure, photographs were taken at 5, 20 and 40 minutes respectively after the elevation of the filament temperature. They grew gradually in the lengthwise direction without changing their diameters, although some one caused the growth suddenly.

In the temperature range of $100\sim 1300^\circ\text{C}$ at 3×10^{-3} mmHg (Photo. 2), the needle crystals shown in Photo. 1 evaporated from their tips and near the roots leaving a single or a few thin needles, and several steps appeared in the side wall. At $1300\sim 1600^\circ\text{C}$ the needle crystals almost evaporated and some lump-like crystals of several thousands Angstroms were formed (Photo. 3). At 1600°C thin films were grown abruptly (Photo. 4) and at about 1800°C they faded away. The diffraction pattern of this thin film showed that it was α -tungsten oxide (WO_3) so perfect as to give clear Kikuchi lines. And above 2000°C all oxide disappeared and the surface became smooth and bright which seemed to be bare metallic surface (Photo. 5).

(b) Case of preliminary heating in air

In the case with preliminary heat-treatment at 500°C in air for an hour, the tungsten filament was covered with a thick sheath of its oxide. Needle crystals were grown up by heating this sample in vacuum of 4×10^{-4} mmHg at 9000°C (Photo. 6). Photographs were taken at 20, 25, 30 and 35 minutes respectively after elevation of temperature. The crystals thus grown are much thinner, as compared with the case shown in Photo. 1, indicating that they had been grown ap-

parently from their tips. It is characteristic in this case that the needle wall has several steps.

(c) Bundle structure of a needle

It can be seen from Photo. 2 that each thick needle crystal was corroded as if individual thin needles constituting the whole needle evaporated independently. It seems to be an evidence supporting the bundle structure of a needle (Fig. 2), which was also confirmed from the high resolution electron diffraction pattern (Photo. 7). Diffraction spots on a series of layer lines perpendicular to the needle axis correspond to oscillation photograph of a single crystal. And as reported previously, the bundle structure is most probable than any other structures.

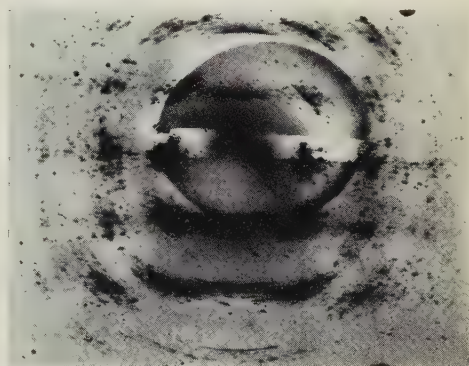


Photo. 7. High resolution electron diffraction pattern from many needle crystals with different orientations, indicating that each needle has bundle structure.

In this structure, many microcrystalline needles are bundled together with their b -axis parallel to the common needle axis, and form a thick needle in which individual needles orient within some angular range less than 30 degrees. In Photo. 8, the diffraction patterns of needles with various diameters are summarized. But, in the patterns given by the needles thinner than 100 Angstroms (c, d, e), the spots from the needles with larger diameters are inevitably included, since it is difficult to pick up thin needles only.

(d) Crystal deformation and the effect of smearing

The electron irradiation for a long time at 1100°C in vacuum of 4×10^{-4} mmHg caused some deformation of the needle (Photo. 9). Several transparent segments of about 200

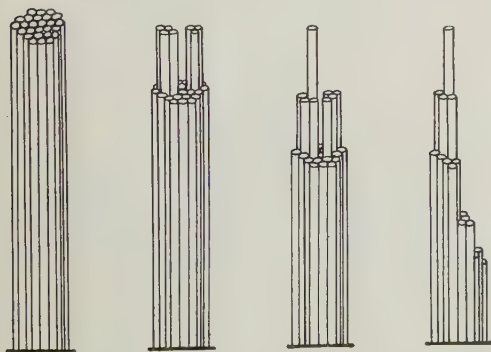
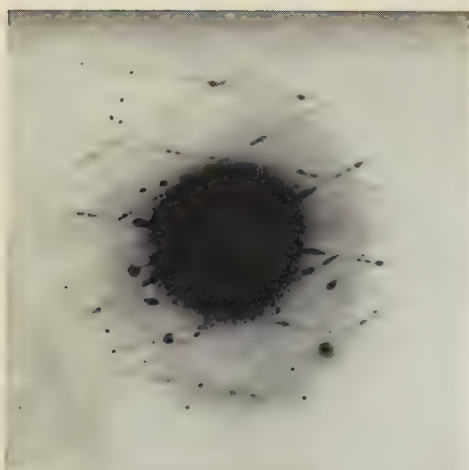
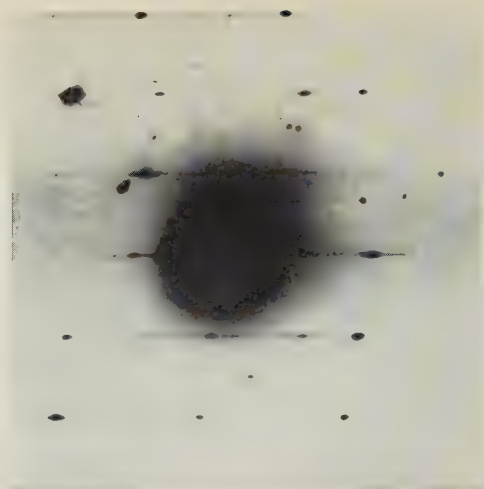


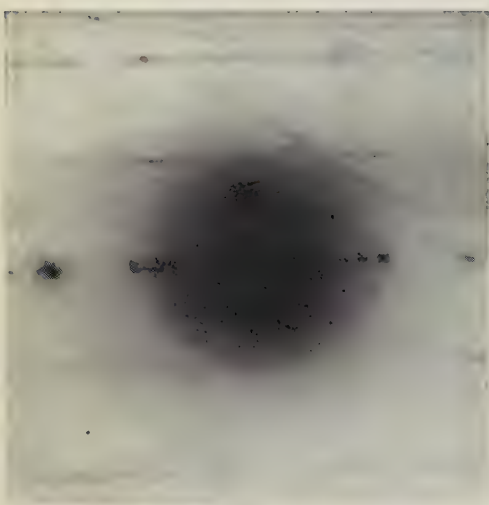
Fig. 2. Bundle structure of tungsten oxide needle crystal.



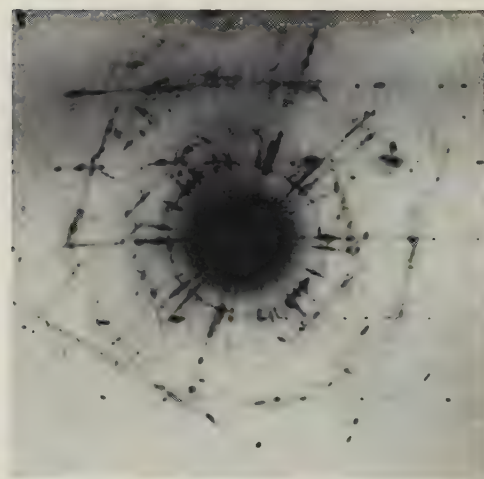
(a)



(b)



(c)



(d)



(e)

(a) 500Å, 130Å

(b) 400Å

(c) 100Å

(d) 80~60Å

(e) 50~30Å

Photo. 8. Diffraction patterns of needles with various diameters.

Angstroms in length appeared in the needle crystal at intervals of 2 or 3 thousands angstroms. Then the needle was broken up into several pieces at these transparent parts by subsequent irradiation. It seems that these weak points are the crystal boundaries formed by some effects of impurities which have been introduced into the crystal during the growth process. The breaking down of the needles also took place when some foreign material attached to them at elevated temperature. An example is given in Photo. 10 in which ZnO smoke was used as a poison.

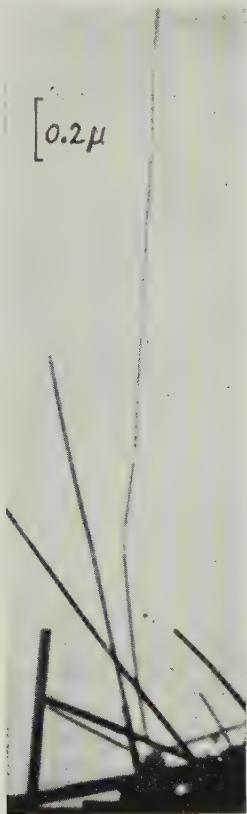


Photo. 9. Deformation of a needle by electron irradiation.

The ZnO fine crystal, condensed onto the needle by evaporation, deformed at 950°C and in 4×10^{-4} mmHg and the fine legs of ZnO crystal twisted together with the tungsten oxide needle, and then the needle broke away at the twisted part, due presumably to some chemical reaction by smearing.

In order to study the possibility of surface and inner migration of supplied growth material, thick smearing by ZnO smoke was given on the surface of the needles (Photo.

11a). And diffraction pattern from the area surrounded by a circle gives only the rings of ZnO crystals. By subsequent heating at higher temperature of 1000°C, the thin needles of tungsten oxide were grown on the crystals of ZnO. The diffraction pattern indicating γ -tungsten oxide was taken from the same area. In this case these thin needles of about 30~50 angstrom in thickness have random orientation. Since they were grown in cluster very rapidly, it seems that the growth material was supplied from the vapour phase.

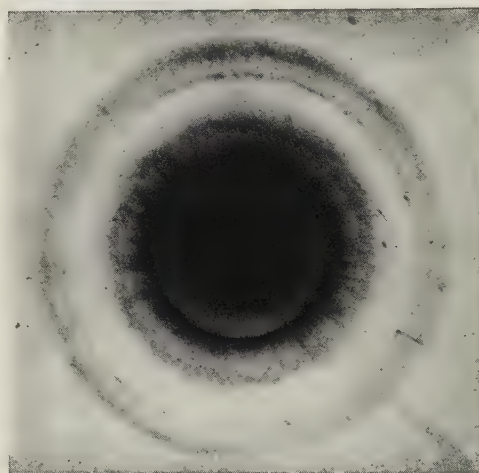
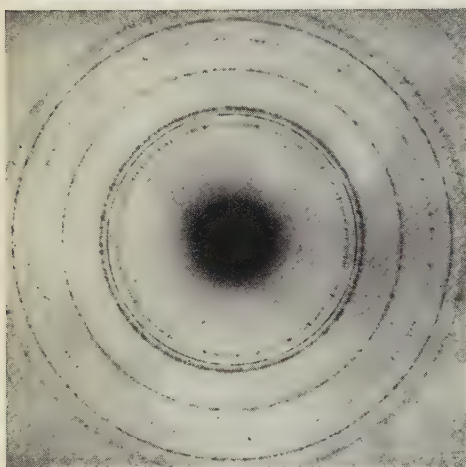


Photo. 10. Deformation of needle by attachment of ZnO smoke at 950°C and 1000°C.

§ 4. Discussions

(a) Growth mechanism

As seen in many other needle crystals of metallic oxides, needles of tungsten oxide also grow from the tips, which will be discussed in the next part (b). For the process of crystal growth, the following three manners would be possible for the supply of growth material: (1) Tungsten atoms or ions are supplied to the tips by diffusion process through the inner part of the needles and they react with oxygen molecules remained



(a)

(b)

Photo. 11. Smearing of needle crystals by ZnO and corresponding diffraction patterns.

(a) ZnO smoke was attached onto the needles.

(b) Needle crystal was held for 10 sec at 1000°C in 4×10^{-4} mmHg.

in vacuum, (2) the metallic tungsten or the tungsten oxide molecules migrate on the needle surface to the tips, (3) condensation of oxide molecules onto the tips of needles from the vapour phase surrounding crystal.

Among these three cases, the case (3) is most suitable in accord with high vapour pressure of tungsten oxide. In the cases (1) and (2) have little importance in the present experimental conditions, because, as can be seen in Photo. 9, the crystal boundary perpendicular to the needle axis should be a high potential barrier for migration of material. And if the reactions of tungsten atoms or ions with oxygen play some important role, the pressure of oxygen in vacuum must give some influence on the growth rate. But any

detectable difference in growth rate could not be observed in different degrees of vacuum (10^{-3} mmHg and 10^{-4} mmHg). The observation of needle growth on smeared crystal (Photo. 11) supports the case (3), as mentioned in the previous section.

There are two possibilities for attaining the stoichiometric composition of needles, that is, $\text{WO}_{2.72}$ (γ -tungsten oxide) in participation of WO_3 vapour molecules, namely:

(1) $\text{W} + \text{WO}_3$;

(2) Reduction of WO_3 .

The case (1) means that WO_3 reacts with tungsten atoms or ions supplied by migration through the needle or by condensation from the vapour phase. In this case, migration of tungsten atoms or ions through the needle

has a difficulty mentioned above, and condensation from the vapour may be impossible owing to the very low vapour pressure of tungsten metal near 900°C . It seems that the trioxide is apt to be reduced in vacuum, as many other multivalent metallic oxides do so, so that the case (2) is more possible.

(b) Growth rates

The relationship between the crystal length and heating time in the case of no preliminary heat-treatment in air is shown in Fig. 3,

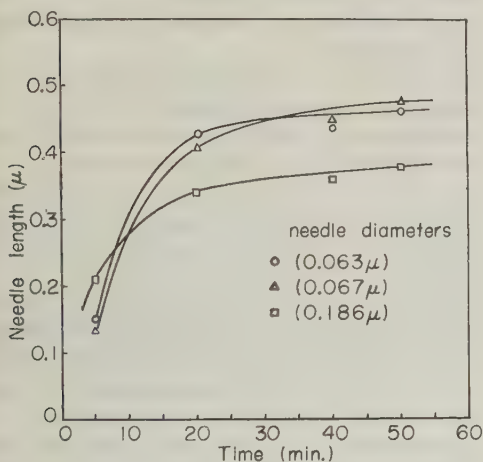


Fig. 3. The relationship between the needle length and heating time, measured from Fig. 2 (without heat-treatment).

for a few needles, which was measured from Photo. 1. In these curves the growth velocity is relatively large within 15 or 20 minutes after beginning of heating, and thereafter decreases gradually, the initial growth velocity being $0.03\sim 0.045\ \mu/\text{min}$. Extrapolating these curves to the zero point of needle length, an induction period can be obtained, which is the time interval necessary for forming a nucleus of needle crystal. It is nearly equal to zero in this case, meaning that the nucleus has existed from the beginning on the filament surface or it has been formed within a time too short to be detected.

Fig. 4 gives the length *versus* time relationship in the case of pre-heated needles with diameters of 0.02 , 0.04 and $0.10\ \mu$ respectively, which was measured from Photo. 6. The growth velocity is of comparable order with that of initial part in Fig. 3. Extrapolation of the curve to zero as before shows that the induction period becomes

again to zero, which is naturally anticipated from Fig. 3, because the nucleus formation should be more easy by preliminary heat-treatment.

The marked decreases of growth velocity in comparison of Fig. 3 with Fig. 4, can be explained as follows. Namely, the oxide molecules to be supplied from the filament surface through the vapour phase are almost evaporated away within $15\sim 20$ minutes, whereas in Fig. 4 the thick oxide layer formed by pre-heating secures the smooth growth of needles.

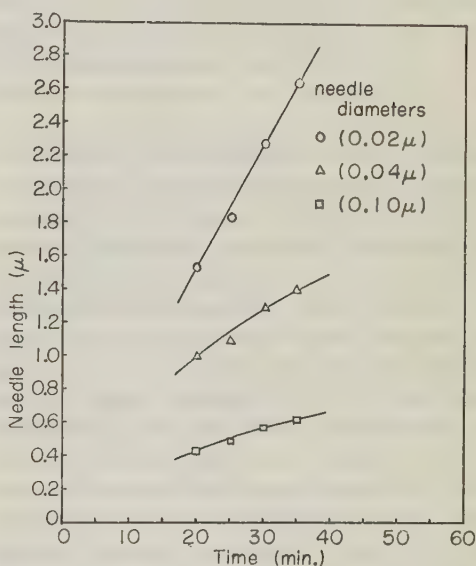


Fig. 4. The relationship between the needle length and heating time, measured from Fig. 7 (without preliminary treatment in air).

The regularity in the growth rates of various needle diameters in Fig. 4 can be accounted for by the following considerations.

We postulate that there exist everlasting sites or steps suitable for growth material to fix on the needle tips. If all the growth materials supplied from the vapour phase within a certain distance from the growth end contribute to the needle growth by surface migration, the total volume of growth material per unit time may be almost proportional to the needle radius. On the other hand, the growth velocity V should be inversely proportional to the square of the radius. Thus the relation between the growth velocity and the needle radius r should be

$$V \propto \frac{1}{r}.$$

Fig. 4 shows a satisfactory agreement with this formula. And the disagreement in the case of Fig. 3 can be understood if we take into account that the oxide layer on the filament surface supplying growth material is so thin that the growth condition can be varied locally on the filament.

(c) *Individual needles and imperfections*

It is estimated that the diameters of individual needles forming a bundled needle crystal is less than 150 angstroms, which corresponds to a thickness less than ten unit cells. We have explained the growth rate in the previous section (b) by postulating that there are sites suitable for fixing the growth material on the needle tips. In the growth conditions realized in the present experiment, the two-dimensional successive nucleation is presumably impossible, considering from the value of vapour pressure. Here the existence of axial screw dislocations in individual needles are recollected. Wilson¹⁵⁾ has discussed this subject theoretically. According to his calculations, the reflections on zero order layer line perpendicular to the screw dislocations are unaffected by the axial screw dislocations, and the spreading of high intensity region appears in the layer lines of higher orders. From the view-point of line spreading the existence of screw dislocations in the needles in the present experiment (Photo. 7) is fairly suspicious.

However, it may be possible that the growth materials are settled in crystal boundaries with small tilt angles formed between individual needles. Or, in the crystal which

has distinct anisotropy like complex oxide, it should not be overlooked the possibility that the variation of surface energy of respective lattice plane is so large as to make some crystal surface to have a deep minimum of surface migration potential or stable molecular sites for supplied molecules.

Anyway, it is most important subject to know the kind and grade of imperfections in the needle crystals.

References

- 1) M. Arnold and E. Koonce: J. Appl. Phys. **27** (1956) 964.
- 2) G. Pfefferkorn: ZS. Metallkunde **46** (1955) 204; Umschau Wiss. Tech. **21** (1954) 654.
- 3) R. Takagi: J. Phys. Soc. Japan **9** (1954) 162; Metal Phys. **1** (1955) 199 (in Japanese).
- 4) T. Morita and T. Seiyama: Oyobuturi **25** (1956) 70 (in Japanese).
- 5) M. Cowley: J. Electro-chem. Soc. **101** (1954) 277.
- 6) *Growth and Perfection of Crystals*, ed. by R. H. Doremus, B. W. Roberts and D. Turubull, (John Wiley and Sons. Inc. New York, 1958).
- 7) R. Takagi: J. Electronmicroscopy **3** (1955) 18.
- 8) B. Borries and E. Ruska: Naturwiss **27** (1939) 281.
- 9) N. Sasaki and T. Kuroda: J. Appl. Phys. Japan **17** (1948) 261 (in Japanese).
- 10) N. Sasaki and R. Ueda: J. Electronmicroscopy **2** (1952) 87 (in Japanese).
- 11) W. Schmidt: Kolloid ZS **15** (1943) 102.
- 12) H. Hashimoto, K. Tanaka and E. Yoda: J. Electronmicroscopy **8** (1958) 6.
- 13) H. Hashimoto, K. Tanaka, E. Yoda and H. Araki: Acta Metal. **557** (1958) 6.
- 14) A. Magneli: Arkiv Kemi. **1** (1949) 234; Analyt. Chem. **24** (1952) 998.
- 15) A. J. C. Wilson: Acta Cryst. **5** (1952) 318.

Dislocations in Pure Iron Foils Deformed by Bending

By Tadayoshi YAMASHITA and Youji TANEDA

*Department of Mathematics and Physics, Defense Academy,
Yokosuka, Japan*

(Received March 4, 1960)

Dislocations in a thin section of a pure iron foil deformed by bending have been observed by transmission electron microscopy. The parallel dislocations up to several μ length or more, presumably intersecting but no degenerating dislocations, loops and half loops of dislocations are found. The average density of dislocations in a well annealed state and in a bent foil are, respectively, $10^8 \sim 10^9/\text{cm}^2$ or less and $10^{11} \sim 10^{12}/\text{cm}^2$. The formation of dislocations due to the bending is concluded from the increase in the density of dislocations and from the stress present in the foil. The three-dimensional arrangement of dislocations in the specimen is proposed to interpret the results obtained. A simple method for the preparation of a thin foil is also developed.

§ 1. Introduction

Since P. B. Hirsch and his co-workers¹⁾ succeeded in observing dislocations in a beaten aluminium foil by transmission electron microscopy, many experiments have been reported on dislocations in annealed and deformed foils,²⁻⁷⁾ in evaporated films,⁸⁾ and in quenched foils of metals.⁹⁾⁻¹¹⁾ Thus, the behaviours of dislocations in a thin foil has been verified in terms of theory of dislocation.

In the course of their investigations on the motion and source of dislocations, Whelan et al.²⁾ applied complicated stress to the rolled foil of stainless steel by using a large beam current and fine focus illumination, whereas A. Berghezan et al.⁷⁾ extended the aluminium foil in tension in the electron microscope. However, it seems to be interesting to examine dislocations in a foil deformed by bending because of the presence of the neutral layer. Besides, it is worth while to make clear the behaviour of dislocations in a metal having body centered cubic lattice, because most of the experiments published hitherto have been done for the metals with face centred cubic lattice.

The purpose of the present experiment is to show the results obtained from the direct

observation of dislocations in α iron foil deformed by bending at room temperature. Especially, the behaviours of long dislocations almost parallel to each other, complete loops, half loops of dislocation lines, and the nucleation of dislocations are examined in details. As for the preparation of thin sections of a metal, a very simple method is developed, which quite differs from W. Bollmann's method¹²⁾ and H. M. Tomlinson's method.¹³⁾

§ 2. Experimental Procedures

The pure iron sheet supplied from Showa Denko Co. was cold rolled down to 7/100 mm thickness. Many strips 11 mm $\times$ 25 mm in size were cut off from the rolled sheet. They were annealed in vacuo at 750°C for 3 hours and furnace cooled. The chemical analyses are given in Table I.

The specimens used in this experiment were prepared by electropolishing the strips. A strip serving as anode was sandwiched between two metal frames, as shown in Fig. 1, of the same material as the strip to be polished, namely iron. The anode was thinned down by electropolishing in a bath of 95% glacial acetic acid and 5% perchloric acid until the strip was perforated in several places

Table I. Analyses of specimen used.

Compositions	C	S	Si	Mn	Ni	Cu	P	O ₂	H ₂	N ₂	Fe
%	0.004	0.005	0.004	0.003	0.005	0.0009	0.0003	<0.0030	<0.00001	trace	>99.97

at the window of the frame. The polishing at a current corresponding to the plateau on the current-voltage curve and at temperature below 30°C of the electrolyte gave good result. The voltage across the electrodes was about 35 V. The strip thus polished was removed from the frames and washed in ethyl alcohol. After dried quickly in vacuum, the deformation by bending was carefully applied to the strip placed between two annealed aluminium plates of about 5/100 mm thickness. Then, the several specimens were cut away with a razor-blade from the deformed or as-annealed foils and each of them was mounted on a 150 mesh copper grid for the direct examination by transmission in the electron microscope.

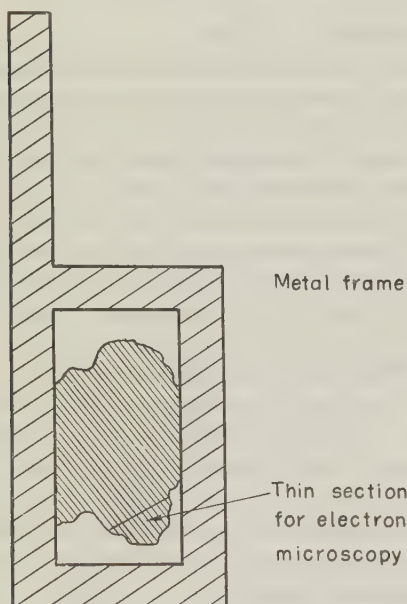


Fig. 1. Frame-shape anode of iron. A strip to be electropolished is sandwiched between these two frames and thinned down until it has been perforated in several places at the window.

Japan Electron Optics Laboratory JEM-5 electron microscope operating at about 90KV was used to observe dislocations existing in the specimen. An objective sperture of about 10μ was used so that Bragg reflections did not contribute to final image. Care was paid not to change the arrangement of dislocations during the observation by illuminating the specimen with an appropriate beam current of electrons. However, a higher beam current was used in order to examine the mo-

tion and rearrangement of dislocations. The electron micrographs at an instrumental magnification of 15,000 and 25,000, bright and dark-field, and the electron diffraction patterns from selected areas, were taken. They were, also, taken at several stages of tilting the specimen through a few degrees in order that the investigation of dislocations could be done more securely.

§ 3. Experimental Results

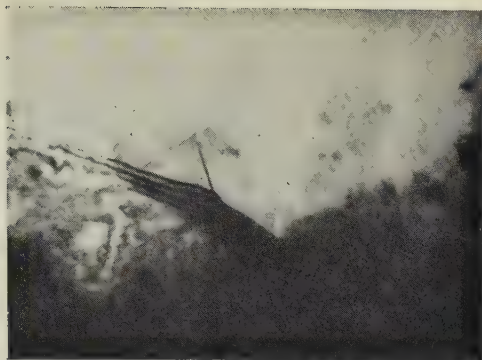
(1) *Texture of specimen as-annealed*

The crystal grains in the annealed strips varied from 8 to 40μ in size and had no preferred orientation according to the optical and X-ray investigations, respectively. The foils prepared by electropolishing were covered by the films consisting mainly of iron hydroxide. The composition of the films was determined from the photographs of the electron diffraction patterns of the films. Precipitations in the foils could seldom be observed both in the grains and in the boundaries, but some very small pin holes about several hundred Å in dia. existed.

There appears to be very few dislocations in the grains. Straight dislocations attached to or close to the grain boundaries can be observed. They indicate the absence of stress in the foil well annealed. One of their typical photographs is shown in Photo 1. Preliminary observations suggests that their density would be 10^6 to $10^8/\text{cm}^2$ or even less in the material annealed at temperature below α to γ transformation (910°C). Sub-structure can not be observed inside a grain in good agreement with the previous experiment on etch pits.¹⁴⁾

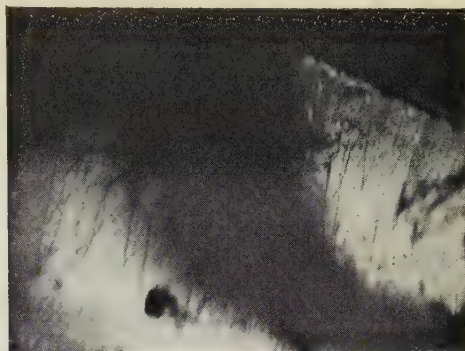
(2) *Arrangement of dislocations due to bending*

Photo 2 and 3 show the arrangement of dislocations inside a grain and Photo 4 the one close to a boundary, in a specimen deformed by bending. In these micrographs almost parallel dislocations up to several μ length or more can be clearly seen near to and in the extinction contours. It is interesting to note that such long dislocations can exist stably in the specimens. Now, two sets of dislocation lines with quite different directions is shown in Photo 3. Some of the dislocation lines would presumably intersect and the others appear to observe the intersection.



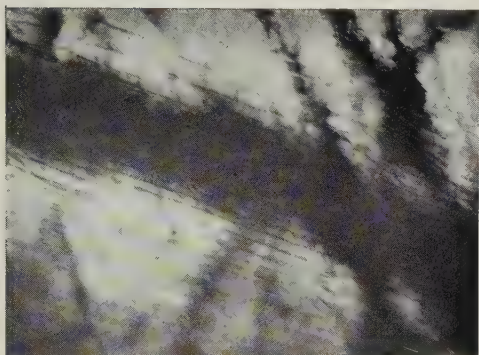
2000 Å

Photo 1. A straight dislocation in an annealed foil. Most of the dislocations observed so far exist in the regions near to the boundaries.



2000 Å

Photo 4. Dislocations near to the boundaries. Many dislocations terminate at the boundary.



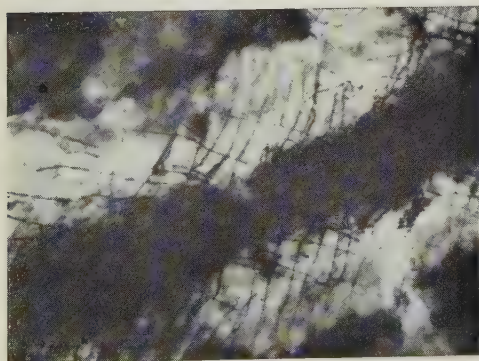
2000 Å

Photo 2. Long dislocations almost parallel to each other, which are observed in a grain of a foil deformed by bending. Black and broad bands are extinction contours.



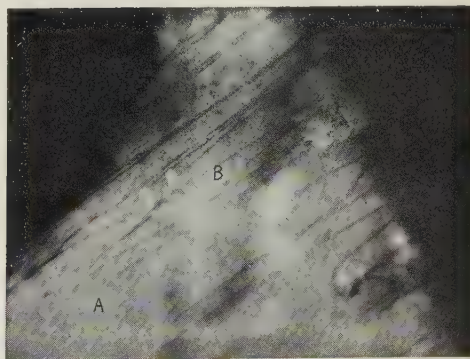
2000 Å

Photo 5. Small loops *L* of dislocation.



2000 Å

Photo 3. Two sets of dislocation lines with different directions. There seems to be no degenerating lines even when the lines intersect.



2000 Å

Photo 6. Arrangement of dislocations near to a boundary. A denotes the half loop and B the dislocation having the end at a surface of a foil.

Those could be, in some cases, deduced by the fact whether the both sets of dislocation lines can be focussed simultaneously by changing the focal length of the objective lens of the electron microscope or not. There are no degenerating dislocation lines even in the case of intersection. The intersecting dislocations would possibly exist at the film-metal interface or just below the hydroxide film, because the strain is maximum at the surface of the bent specimen.

In addition to the dislocations shown in these photographs, the micrographs of the various types of dislocations such as shown in Photo 5, 6 and 7 were frequently taken. Photo 5 shows the small dislocation loops whose minimum radius of curvature in the slip plane is about $250\text{\AA}$. The stress σ acting on the loop, for which the bending of the specimen is responsible, can be calculated from the relation $\sigma = bG/2r$,²⁾ where b is Burgers vector, G the shear modulus and r the radius of curvature of the loop. The estimated value is about $G/210$, by taking the values $b=2.4\text{\AA}$ and $r=250\text{\AA}$. This stress present in a foil is hundred times higher in value than the flow stress of the bulk material.

Photo 6 shows the half loop A of dislocation line. It is not clear whether a loop has originated at the boundary and grown into the grain or it has nucleated inside the grain and extended to the boundary. Further, there is a dislocation line B whose end terminates in the area of the figure. Judging from the property of dislocation which should

not have the ends inside a crystal, middle parts of the dislocation line would exist near to the neutral layer of the bent specimen and the both ends would emerge at the surface, in stead of lying always just below the film.

Photo 7 shows the many lines bowing sharply and rather regularly. Among them two lines parallel to each other and bowing at the same place, for example A and B, imply that they are two components of a loop, and that the one of them must lie at the surface of the foil and the other in the region near to the neutral layer. Each part of a bent line would not lie in one slip plane, but in the conjugate slip planes since dislocation line in



Photo 8. Arrangement of dislocations in exactly the same area as in Photo 2 after strong illumination with a higher beam current of electrons. It is scarcely observed for dislocations to move or to annihilate by the strong illumination.

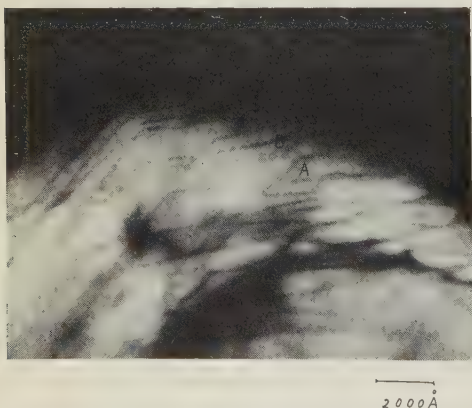


Photo 7. Regularly bent dislocations which supposed to be cross slip. Dislocations A and B will correspond to the two components of a dislocation loop.

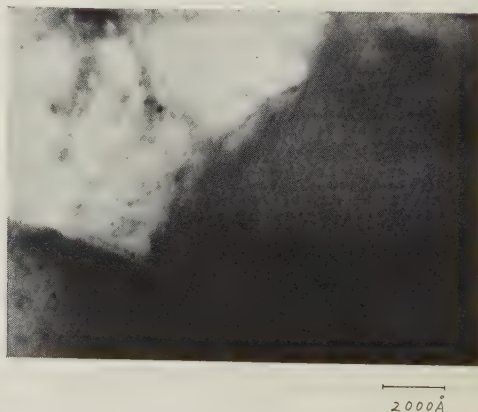


Photo 9. Apparently indistinct dislocations because of the shift of the extinction contour by illumination. Most of the dislocations correspond to the ones in Photo 4.

one slip plane has a nature which tends to be straight to lower its energy unless strong obstacles interrupt to be short. Thus, the bent line is supposed to show cross slip. Many occurrences of the bends of dislocation line suggest the feasibility of cross slip in iron in good agreement with the results obtained previously.¹⁵⁾

The average density $10^{11} \sim 10^{12}/\text{cm}^2$ of dislocations is obtained from the many micrographs, taking into consideration of the average thickness of the foil. The exact thickness concerned can not be measured in this experiment, because it is very difficult to make the dislocations slip in order to calculate the thickness of the foil (cf. 3). However, the thickness desired can be estimated from the width of slip of a dislocation in the foil prepared by electropolishing the stretched specimen, because thickness suitable for observing dislocations does not vary in order of magnitude in both cases. The details of the experiment on dislocations in a foil stretched in tension will be published elsewhere.

(3) *Effect of heating on dislocations*

In order to investigate the motion and annihilation of dislocation by stress and temperature, the foil was tried to illuminate with a higher beam current of electrons after the observations described above had been finished. A part of the specimen was heated up immediately below the $\alpha \rightarrow \gamma$ transformation temperature. The temperature of the specimen was deduced by the fact that the transformation of specimen was accomplished in the field of view under investigation by the increase of the very small amount of a beam current. Thus, the micrographs, Photo 8 and 9 were respectively taken from the same area as Photo 2 and 4 after the strong illumination.

The extinction contours are displaced from their original positions and also change their appearances because of the variation of the buckling of the foil. Nevertheless, it is scarcely observed for dislocations to move or to annihilate as seen from these figures. Dislocations are kept remained even when they can not be clearly seen after strong illumination. The displacement of the extinction contours causes merely the difficulty in observing dislocations. In such cases dislo-

cations enable to show themselves up again by tilting the specimen adequately. There is a question whether the difficulty in motion of dislocations is attributed to the kinds of deformation such as bending and tension, or to the crystal structure of α iron having body centered cubic lattice. Thus, the experiments for the specimens stretched in tension have been done as mentioned above. The answer is that such a difficulty in motion arises from the bending of the specimen, but not from the crystal structure, because dislocations in stretched specimen can rearrange easily to make sub-boundaries and can, also, move by leaving the dislocations at the both surfaces of the foil.

§ 4. Interpretation of Results

(1) *Nucleation of dislocations*

Most of the dislocations in the annealed specimen are observed in the region near to the boundary instead of existing inside the grain, and the average density is $10^6 \sim 10^8/\text{cm}^2$ or even less. On the other hand, dislocations in the foil deformed by bending exist inside the grain as well as closely to the boundary, and their average density is $10^{11} \sim 10^{12}/\text{cm}^2$, which shows the increase in value more than four orders of magnitude. No micrographs as shown multiplication of dislocations from Frank-Read source are taken up to now. Consequently, such increase may be attributed to (A) the growing probability, in observing dislocations, due to the buckling of the foil, (B) the movement of dislocations by bending into the thin sections from the thicker parts through which an electron beam hardly transmits, and (C) nucleation of dislocations. The increase from (A) can be estimated roughly by the experiment of tilting the specimen and the one from (B) by extrapolating the density of dislocation in the thicker part of the specimen from the density in the thin section, taking into account that each dislocation leaves two components of half loop of dislocation by slip. These estimations may account for the increase by one order of magnitude at most. Thus, it can be concluded that the dislocations should nucleate in the thin foil or from the surface of the foil. However, there seems to be two mechanisms for dislocation loops to be nucleated; (a) dislocation loop formed by the

coalescence of vacancies created from the intersection of dislocations and (b) dislocation loop nucleated by the slip due to the action of the applied stress. In the former case, dislocation density more than $10^{13}/\text{cm}^2$ will be necessary to form dislocation loops with $250\text{\AA}$ radius in the foil of $500\text{\AA}$ thickness. It is impossible for the dislocation loops to nucleate by the former mechanism, because the dislocation density in the annealed foil is smaller than $10^9/\text{cm}^2$. Therefore, it is believed that the dislocation loops nucleate from the mechanism of the latter case. This conclusion can, also, be supported from the result which the maximum stress acting on dislocation line is about $G/200$ as described before. Cottrell¹⁶⁾ have pointed out that slip can not be nucleate unless the stress exceed $G/100$, which is two times larger than ours. Since the observed loop has the larger radius of curvature than the critical size at which the loop begins to grow by the applied stress, it is reasonable to consider that the stress larger than $G/100$ would be submitted to nucleate dislocation to the foil while bending.

Furthermore, M. J. Whelan et al.²⁾ have observed the nucleation of dislocation in a wedge crystal such as occurs near a hole in the foil. In the present experiment, dislocations are observed to increase by bending in a wedge crystal as well as in a crystal with uniform thickness where there is no hole at all. However, in the former case, dislocation can nucleate at much lower stress of $G/800$, which is smaller by a factor of four than ours.

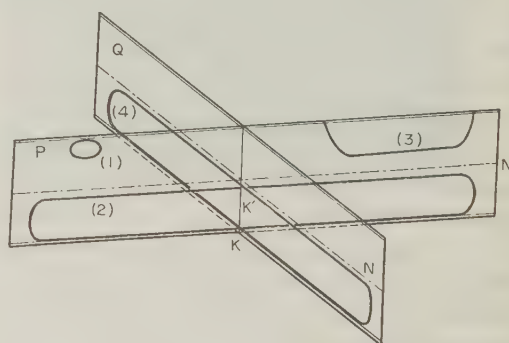
(2) Configuration of dislocations

In a bent foil there are many types of dislocations, such as complete loops, half loops, parallel dislocations up to several μ length or more, intersecting dislocations, dislocation lines having their ends at the surface of the foil, and the ones with sharp bends. These dislocations are characteristic for a bent foil.

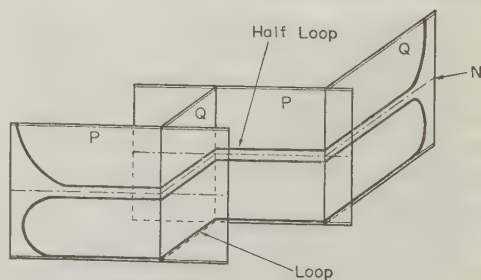
From the results already described the three dimensional arrangement of such dislocations can be considered as shown in Fig. 2, where P and Q denote the primary and conjugate slip planes¹⁷⁾ in a crystal, respectively. There are neutral layer N at the middle part of the foil, and films mainly consisted of hydroxide occupy both top and bot-

tom surfaces. The small loop (1), the larger one (2) a part of which is pinned at the surface of the foil, half loop (3) whose both ends are anchored at a surface or at a crystal boundary, and the loop (4) existing in the conjugate slip planes are drawn schematically in Fig. 2(a). The dislocations in the planes conjugate to each other may intersect at K because the stress at the surface is maximum, but do not necessarily intersect at K' near to the neutral layer N as the shear stress acting on the dislocation in the slip plane P differs from that in the plane Q .

Now, the small loop nucleated in the foil grows under the applied stress. If there is an obstacle which the tip of the growing loop can not surmount, the loop comes out of the original slip plane and goes into the other. Thus cross slip takes place as shown in Fig. 2(b), where cross slip for the two types of dislocations, namely complete loop and half



(a)



(b)

Fig. 2. Proposed arrangement of dislocations written pictorially.

(a) Complete loops (1) and (2), half loop (3), and loop (4) intersecting at K , but not necessarily intersecting at K' with the loop (2). P and Q are primary and conjugate slip planes respectively. N denotes a neutral layer.

(b) Bent dislocation lines showing cross slip.

loop, are indicated. These are somewhat similar to the idea of double cross slip proposed by J. R. Low et al.¹⁸⁾ provided no multiplication of dislocation takes into consideration.

In conclusion, our thanks are due to Prof. T. Fujiwara and Prof. T. Suzuki for their continued interest and advice during the course of this experiment.

References

- 1) P. B. Hirsch, R. W. Horne, and M. J. Whelan: *Phil. Mag.* **1** (1956) 677.
- 2) M. J. Whelan, P. B. Hirsch, R. W. Horne and W. Bollmann: *Proc. Roy. Soc. A*, **240** (1957) 524.
- 3) D. G. Brandon and J. Nutting: *Acta Met.* **7** (1959) 101.
- 4) G. Thomas: *Phil. Mag.* **4** (1959) 606.
- 5) P. B. Hirsch, P. G. Partridge and R. L. Segall: *Phil. Mag.* **4** (1959) 721.
- 6) Z. Nishiyama, A. Koreeda and K. Shimizu: *J. of Electron-microscopy* **7** (1959) 41.
- 7) A. Berghezan and A. Fourdeux: *Compt. rend.* **248** (1959) 1333.
- 8) D. W. Pashley: *Phil. Mag.* **4** (1959) 324.
- 9) P. B. Hirsch and J. Silcox: *Phil. Mag.* **3** (1958) 897.
- 10) G. Thomas and M. J. Whelan: *Phil. Mag.* **4** (1959) 511.
- 11) J. Silcox and P. B. Hirsch: *Phil. Mag.* **4** (1959) 72.
- 12) W. Bollman: *Phys. Rev.* **103** (1956) 1588.
- 13) H. M. Tomlinson: *Phil. Mag.* **3** (1958) 867.
- 14) Y. Taneda and T. Yamashita: *Electron-microscopy* **8** (1959) 63 (in Japanese).
- 15) T. Yamashita and Y. Taneda: *Electron-microscopy* **8** (1959) 160 (in Japanese).
- 16) A. H. Cottrell: *Dislocations and Plastic Flow in Crystals* (Oxford Univ. Press, 1953) 53.
- 17) S. Dohi and T. Yamashita: *J. Sci. Hiroshima Univ. Series A*, **22** (1958) 233.
- 18) J. R. Low Jr. and R. W. Guard: *Acta Met.* **7** (1959) 171.

Dynamical Theory of Electron Diffraction in Laue-case,

III. Forbidden Reflection

By Fuminori FUJIMOTO

*Institute of Physics, College of General Education,
University of Tokyo, Komaba, Meguro-ku, Tokyo*

(Received January 9, 1960)

The intensity of the forbidden 222-reflection of electrons from germanium at the Bragg position is calculated as the function of the crystal thickness by means of three kinds of approximation, i.e. (1) exact solution in the harmonic potential corresponding to the 111-Fourier potential, (2) Feynman expansion of the scattering matrix for the harmonic potential taking account of the influence of the 333-Fourier potential, and (3) expansion of the scattering matrix taking account of the three waves (000), (111) and (222).

The integrated intensities of the 222-reflection due to systematic interactions and the 200-reflection due to accidental interactions are also calculated by the expansion of the scattering matrix. The results show that the ratio of the integrated intensity of the 222-reflection to that of the 111-reflection is proportional to the square of crystal thickness and of wave length, and the ratio of the integrated intensity of the 200-reflection to that of the 222-reflection is independent of wave length.

§ 1. Introduction

The appearance of the forbidden reflections in electron diffraction has been often reported for single crystals. Raether¹⁾ explained this appearance by the double reflections between allowed reflections. Germer²⁾ reported that the fairly strong 222-reflections appear also in Debye patterns from CuCl and CaF₂ films in spite of vanishingly small structure amplitudes of these reflections.

Heidenreich³⁾ observed the 222-reflection from germanium, which is forbidden by the space group symmetry, appearing in Debye patterns as well as in single crystalline patterns. He showed theoretically that the strong intensity of the 222-reflection is expected as the result of the *accidental* interactions between 311- and $\bar{1}11$ -reflections. On the other hand, Hoerni⁴⁾ pointed out that the *systematic* interactions are important in germanium for which the Fourier coefficient of potential v_{111} is of considerable magnitude. Since for germanium $v_{222}=0$ and v_{333} , v_{444} etc. are small, he assumed that the potential variation in the direction [111] can be approximated by a harmonic potential, and showed, by the use of a "Mathieu function", which is the exact solution of the Schrödinger equation for harmonic potential, that the 222-reflection of germanium may be fairly strong

at arbitrary crystal azimuth even if the condition for the accidental interactions for 311- and $\bar{1}11$ -reflections is not satisfied.

The forbidden reflections such as 200- and 420-reflections of germanium, on the other hand, are expected to arise only from the accidental interactions. In fact, it has been observed experimentally that the intensities of these reflections in Debye patterns are very weak compared with that of the 222-reflection⁵⁾.

The purpose of this paper is to study the dependence of the intensity of the forbidden reflections on the crystal thickness and wave length, using the scattering matrix presented in previous paper^{6)*}. Firstly, we discuss, using the Feynman expansion, the intensity of the 222-reflection in the Bragg position by taking account of the influence of v_{333} , which is not taken into account in the treatment assuming the harmonic potential. Secondly, we study the integrated intensity of the 222-reflection taking account of the systematic interactions, and that of the 200-reflection assuming the condition of the accidental interactions.

* In the following, Part I and II are referred to as I and II, respectively. Equations and Sections in Part I are cited by adding I, such as (10-I) and Section 2-I etc.

§ 2. Intensity of 222-Reflection at Bragg Position

In II, we have deduced the formula for the amplitude of reflection by the use of the "Feynman expansion" of the scattering matrix. Let us apply the formula (17-II) to the 222-reflection of germanium.

Considering only the systematic interactions between the hhh -reflections, we have

$$M = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & p_{-2} & v_{-1} & v_{-2} & v_{-3} & v_{-4} & \ddots \\ \ddots & v_1 & p_{-1} & v_{-1} & v_{-2} & v_{-3} & \ddots \\ \ddots & v_2 & v_1 & p_0 & v_{-1} & v_{-2} & \ddots \\ \ddots & v_3 & v_2 & v_1 & p_1 & v_{-1} & \ddots \\ \ddots & v_4 & v_3 & v_2 & v_1 & p_2 & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}$$

where v_h abbreviates $v_{h,h,h}$. When the 222-reflection is in the Bragg position, p_g is given by

$$p_g = -(g-1)^2 b_{111}^2$$

from (27-I), where $b_{111} = 2\pi/d_{111}$.†

For germanium, $v_2=0$ and we may put $v_h=v_{-h}$. In order to study the effect of v_3 on the 222-reflection, we may neglect $v_4, v_5, \dots$. Then, we may put

$$I_{222} = \left| \sum_i \phi_{2(0)}^i \phi_{0(0)}^i \exp\left(i \frac{D}{2k} x_{(0)}^i\right) + \sum_{i,j} \sum_{|g-i|=3} \phi_{2(0)}^i \phi_{g(0)}^i \phi_{l(0)}^j \phi_{0(0)}^j v_3 \left[\frac{\exp\left(i \frac{D}{2k} x_{(0)}^i\right)}{x_{(0)}^i - x_{(0)}^j} + \frac{\exp\left(i \frac{D}{2k} x_{(0)}^j\right)}{x_{(0)}^j - x_{(0)}^i} \right] \right|^2, \quad (1)$$

where $x_{(0)}^i$ and $\phi_{g(0)}^i$ are the eigen value and the component of the normalized eigen vector

Table. Values of eigen values $x_{(0)}^i$ and the components of normalized eigen vectors $\phi_{g(0)}^i$ of matrix M_0 at the Bragg position of 222-reflection from Ge ($v_{111}/b_{111}^2=0.563$).*

i	$x_{(0)}^i/b_{111}^2$	$\phi_{1(0)}^i$	$\phi_{2(0)}^i$	$\phi_{3(0)}^i$	$\phi_{4(0)}^i$	$\phi_{5(0)}^i$	$\phi_{6(0)}^i$
1	+0.45681	+0.86544	+0.35142	+0.04469	+0.00267	+0.00009	+0.00000
2	-0.89674	0	-0.69543	-0.12767	-0.00888	-0.00033	-0.00000
3	-1.34817	+0.49961	-0.59872	-0.12901	-0.00951	-0.00037	-0.00000
4	-4.03995	0	-0.12785	+0.69095	+0.07876	+0.00371	+0.00008
5	-4.04532	+0.03732	-0.13421	+0.68927	+0.07867	+0.00371	+0.00010
6	-9.01811	0	-0.00556	+0.07913	-0.70034	-0.05658	-0.00197
7	-9.01811	+0.00069	-0.00560	+0.07914	-0.70028	-0.05658	-0.00199

* $\phi_{g(0)}^i = \phi_{2-g(0)}^i$ for odd i , and $\phi_{g(0)}^i = -\phi_{2-g(0)}^i$ for even i .

† As shown in I, p_g is defined by the following equation, namely

$$k^2 - k_g^2 = -x + p_g, \quad (7-I)$$

where x is the eigen value of M and is the parameter determining the position of the dispersion surface.

$$M = M_0 + M',$$

where

$$M_0 = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & p_{-2} & v_{-1} & & & & 0 \\ \ddots & v_1 & p_{-1} & v_1 & & & \\ \ddots & & v_1 & p_0 & v_1 & & \\ \ddots & & & v_1 & p_1 & v_1 & \\ \ddots & & & & v_1 & p_2 & \ddots \\ \ddots & & & & & \ddots & \ddots \end{pmatrix}$$

and

$$M' = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & 0 & 0 & v_3 & & & 0 \\ \ddots & 0 & 0 & 0 & 0 & v_3 & \\ \ddots & 0 & 0 & 0 & 0 & 0 & v_3 \\ \ddots & v_3 & 0 & 0 & 0 & 0 & 0 & v_3 \\ \ddots & & v_3 & 0 & 0 & 0 & 0 & \\ \ddots & & & v_3 & 0 & 0 & 0 & \\ \ddots & & & & 0 & v_3 & 0 & 0 & 0 & \ddots \end{pmatrix}$$

M_0 being the unperturbed matrix which corresponds to a crystal with harmonic potential treated by Hoerni. In this case, the intensity of the 222-reflection given by the first and the second terms of (17-II) is written as

of M_0 , respectively. The values of $x_{(0)}^i$ and $\phi_{g(0)}^i$ for Bragg position, which are tabulated in Table, can be obtained by utilizing the table of Mathieu solutions⁷⁾. It must be remembered in the calculation that the terms for $i=j$ in the second term in (1) become

$$i \frac{D}{2k} \sum_i \sum_{\substack{g, l \\ |g-l|=3}} \phi_{2(0)}^i \phi_{g(0)}^i \phi_{l(0)}^i \phi_{0(0)}^i v_3 \exp \left(i \frac{D}{2k} x_{(0)}^i \right).$$

In the numerical calculation, we use the values

$$v_{111}/b_{111}^2 = 0.563 \quad \text{and} \quad v_{333}/b_{111}^2 = -0.184,$$

which are obtained from the value of f_e for germanium given by Ibers⁸⁾.

In Fig. 1, Curve 1 represents the intensity of the 222-reflection in the Bragg position calculated by (1). Curve 2 and 3 are given for comparison, of which Curve 2 represents the intensity obtained by assuming the harmonic potential, namely

$$I_{222} = \left| \left[\exp \left(i \frac{D}{2k} M_0 \right) \right]_{20} \right|^2, \quad (2)$$

and Curve 3, that given by

$$\begin{aligned} I_{222} = & \frac{1}{4} \left(\frac{D}{2k} \right)^4 v_1^4 - \frac{1}{12} \left(\frac{D}{2k} \right)^6 \left(v_1^2 + \frac{1}{6} b_{111}^4 \right) v_1^4 \\ & + \frac{1}{80} \left(\frac{D}{2k} \right)^8 \left(v_1^4 + \frac{1}{3} v_1^2 b_{111}^4 + \frac{1}{36} b_{111}^8 \right) v_1^4 + \dots, \end{aligned} \quad (3)$$

which represents the expansion on the scattering matrix taking account of the waves, 0, 111 and 222.

§ 3. Integrated Intensity of 222-Reflection

For the sake of comparison with the experimental results, it is necessary to calculate the integrated intensity. According to the observation of Germer, the ratio of the integrated intensity of the 222-reflection to that of the 111-reflection has not the linear relation with the grain size. It is interest to study the relation between the integrated intensity and the crystal thickness applying our theory.

The intensity profile of the reflection for which $v_h=0$ is given by (20-I) as follows:

$$\begin{aligned} I_h = & \frac{1}{4} \left(\frac{D}{2k} \right)^4 \left(\sum_g' v_{h-g} v_g \right)^2 - \frac{2}{6!} \left(\frac{D}{2k} \right)^6 \left[15 \sum_g' v_{h-g} v_g \left\{ \sum_{\substack{g, l, m \\ g \neq l, l \neq m}} v_{h-g} v_{g-l} v_{l-m} v_m \right. \right. \\ & \left. \left. + 2 \sum_g' v_g^2 \sum_g' v_{h-g} v_g + \sum_{\substack{g, l \\ g \neq l}}' (p_g + p_l) v_{h-g} v_{g-l} v_l + \sum_g' p_g^2 v_{h-g} v_g \right\} \right. \\ & \left. - 10 \left\{ \left(\sum_{\substack{g, l \\ g \neq l}}' v_{h-g} v_{g-l} v_l \right)^2 + \left(\sum_g' p_g v_{h-g} v_g \right)^2 + 2 \sum_{\substack{g, l \\ g \neq l}}' v_{h-g} v_{g-l} v_l \sum_g' p_g v_{h-g} v_g \right\} \right. \\ & \left. - 5 \sum_g' v_{h-g} v_g \left\{ (p_0 + p_h) \sum_{\substack{g, l \\ g \neq l}}' v_{h-g} v_{g-l} v_l + (p_0 + p_h) \sum_g' p_g v_{h-g} v_g \right. \right. \\ & \left. \left. - (p_0^2 - p_0 p_h + p_h^2) \sum_g' v_{h-g} v_g \right\} \right] + \dots \end{aligned} \quad (4)$$

The term of $(D/2k)^2$ vanishes and the term of $(D/2k)^4$ is independent of the direction of in-

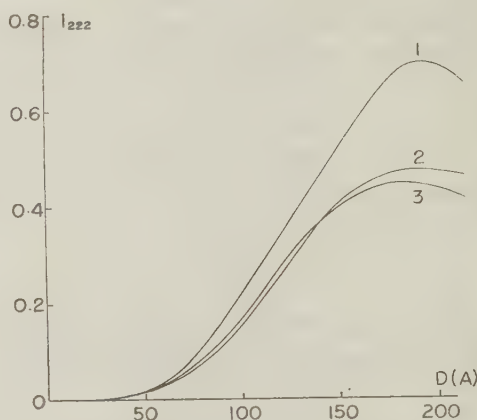


Fig. 1. Intensities of the 222-reflection of Ge at Bragg position obtained by (1) Feynman expansion of the scattering matrix for the harmonic potential taking account of the influence of v_{333} , (2) harmonic potential and (3) expansion of the scattering matrix for three waves, where $k=100\text{\AA}^{-1}$.

cident beam.

For germanium, v_1 is finite and $v_2=0$. So long as the integrated intensity of the 222-reflection is concerned, the systematic interactions are more important than the accidental interactions, as will be understood in Section 5. Accordingly, we consider here only the systematic interactions, taking account of the three waves 0, 111 and 222. If we adopt

$$p_g = -[(g-1)b_{111} - s]^2,$$

where s is the deviation of wave point from the Bragg position of the 222-reflection (see 27-1 and Fig. 2-I) Neglecting the higher terms, we get

$$I_{222} = \frac{1}{4} \left(\frac{D}{2k} \right)^4 v_1^4 - \frac{1}{12} \left(\frac{D}{2k} \right)^6 \left\{ v_1^2 + \frac{1}{6} b_{111}^4 \right\} v_1^4 - \frac{1}{6} \left(\frac{D}{2k} \right)^6 v_1^4 b_{111}^2 s^2. \quad (5)$$

Integrating (5) in a similar way as in I, the integrated intensity is given by

$$\begin{aligned} J_{222} &= \int I_{222} d\alpha = \frac{1}{k} \int_{-s_0}^{s_0} I_{222} ds \\ &= \frac{\sqrt{6}}{6} \frac{v_1^4}{k b_{111}} \left(\frac{D}{2k} \right)^3 \left\{ 1 - \frac{1}{3} \left(\frac{D}{2k} \right)^2 \left(v_1^2 + \frac{1}{6} b_{111}^4 \right) \right\}^{3/2}, \end{aligned} \quad (6)$$

where the integration is performed over the range of s , within which the value of I_{222} given by (5) is positive; $s=s_0$ being the zero point of I_{222} . When $D/2k$ is small, (6) is rewritten as

$$J_{222} = \frac{\sqrt{6}}{6} \frac{v_1^4}{k b_{111}} \left(\frac{D}{2k} \right)^3 \left\{ 1 - \frac{1}{2} \left(\frac{D}{2k} \right)^2 \left(v_1^2 + \frac{1}{6} b_{111}^4 \right) \right\}. \quad (7)$$

For comparison with experiment, the calculation of J_{222}/J_{111} should be useful. It is conceived that the two-wave approximation is fairly accurate for the 111-reflection, since $v_{222}=0$. In the usual calculation of the intensity based on the two-wave approximation, the integration of intensity is carried out over s from $-\infty$ to ∞ ⁹⁾. For the calculation of J_{222}/J_{111} , however, it may be better to apply for J_{111} the same approximation as is used in deriving J_{222} , i.e. expressing the intensity in a quadratic formula and integrating it with respect to s over range $I_{111} \geq 0$. Then we get

$$J_{111} = \frac{4\sqrt{3}}{3} \frac{v_1^2}{k b_{111}} \left(\frac{D}{2k} \right) \left\{ 1 - \frac{1}{2} \left(\frac{D}{2k} \right)^2 v_1^2 \right\}. \quad (8)$$

From (7) and (8), the ratio J_{222} to J_{111} is given by

$$\frac{J_{222}}{J_{111}} = \frac{\sqrt{2}}{8} v_1^2 \left(\frac{D}{2k} \right)^2 \left\{ 1 - \frac{1}{12} \left(\frac{D}{2k} \right)^2 b_{111}^4 \right\}. \quad (9)$$

This result indicates that the ratio J_{222} to J_{111} is proportional to $(D/2k)^2$ when $D/2k$ is small.

Fig. 2 shows J_{222}/J_{111} as the function of D ($k=100 \text{ \AA}^{-1}$). Curve 1 represents the value given by (9), and Curve 2, that of the first term of (9), and Curve 3, that given by*

* The reason for considering (10) is as follows. According to the result of Blackman⁹⁾, the integrated intensity deduced by the two-wave approximation is given by

$$J_h = \frac{2v_h}{k b_h} \int_0^{(D/2k)v_h} J_0(2x) dx = \frac{2v_h^2}{k b_h} \left(\frac{D}{2k} \right) \left\{ 1 - \frac{1}{3} \left(\frac{D}{2k} \right)^2 v_h^2 + \dots \right\}. \quad (8')$$

On the other hand, by the same procedure as is used in deriving (7) (quadratic approximation), we get

$$J_h = \frac{4\sqrt{3}}{3} \frac{v_h^2}{k b_h} \left(\frac{D}{2k} \right) \left\{ 1 - \frac{1}{2} \left(\frac{D}{2k} \right)^2 v_h^2 \right\}. \quad (8'')$$

The difference between (8') and (8'') lies not only in the numerical factor $4\sqrt{3}/3$ but in the coefficient of $(D/2k)^2$ in the curly bracket. These numerical values depend on the order of approximation. The calculation of J_{222} without the quadratic approximation is highly tedious. If we assume that the value of J_{222} calculated in this way has the same numerical factor and the same coefficient of $(D/2k)^2$ in the curly bracket as those in (8'), we obtain (10).

$$\frac{J_{222}}{J_{111}} = \frac{\sqrt{2}}{8} v_1^2 \left(\frac{D}{2k} \right)^2 \left\{ 1 - \frac{1}{18} \left(\frac{D}{2k} \right)^2 b_{111}^4 \right\}. \quad (10)$$

§ 4. Integrated Intensity of 200-Reflection

The 200- and 420-reflections of germanium can arise only from the accidental interactions. Let us study the 200-reflection as an example of the forbidden reflection due to this kind of interactions. Among many types of double reflections which may give rise to the 200-reflection, the most important is the reflections 111 followed by $\bar{1}\bar{1}\bar{1}$ and the reflections $\bar{1}\bar{1}\bar{1}$ followed by 111. In this section, we consider first the interaction between 111- and $\bar{1}\bar{1}\bar{1}$ -reflections.

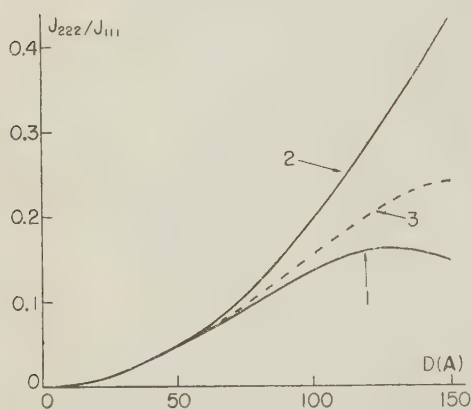


Fig. 2. Integrated intensity ratio of 222-reflection to 111-reflection of Ge. (1) value given by Eq. (9), (2) the first term of Eq. (9) and (3) value given by Eq. (10), where $k=100\text{\AA}^{-1}$.

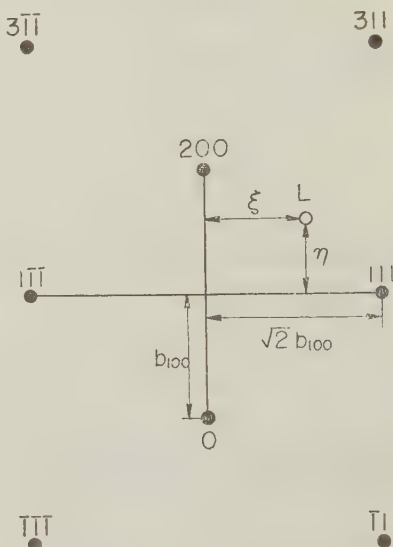


Fig. 3. Reciprocal lattice space relating to 200-reflection.

The geometry of the reciprocal lattice points concerned is shown in Fig. 3. Indicating the position of wave point L by (ξ, η, k_v) , where k_v is the normal component of wave vector of the primary wave, we have

$$\left. \begin{aligned} p_{000} &= -(\xi^2 + \eta^2 + 2b_{100}\eta) \\ p_{200} &= -(\xi^2 + \eta^2 - 2b_{100}\eta) \\ p_{111} &= -(\xi^2 + \eta^2 - 2\sqrt{2}b_{100}\xi + b_{100}^2) \\ p_{\bar{1}\bar{1}\bar{1}} &= -(\xi^2 + \eta^2 + 2\sqrt{2}b_{100}\xi + b_{100}^2) \end{aligned} \right\} \quad (11)$$

Substituting (11) into (4) and using

$$v_{111} = -v_{\bar{1}\bar{1}\bar{1}} \quad \text{and} \quad v_{022} = v_{\bar{0}\bar{2}\bar{2}},$$

we obtain

$$I_{200} = \left(\frac{D}{2k} \right)^4 v_{111}^4 - \frac{1}{18} \left(\frac{D}{2k} \right)^6 (v_{022}^2 + 12v_{111}^2 - 2v_{022}b_{100}^2 + b_{100}^4) v_{111}^4 - \frac{2}{3} \left(\frac{D}{2k} \right)^6 v_{111}^4 b_{100}^2 (2\xi^2 + \eta^2). \quad (12)$$

When we integrate (12) with ξ and η in the region where I_{200} given by (12) is positive, we obtain the integrated intensity of the 200-reflection as follows:

$$\begin{aligned} J_{200} &= \frac{4}{4\pi k^2} \int I_{200} d\xi d\eta \\ &= \frac{3\sqrt{2}}{8} \frac{v_{111}^4}{k^2 b_{100}^2} \left(\frac{D}{2k} \right)^2 \left\{ 1 - \frac{1}{18} \left(\frac{D}{2k} \right)^2 (v_{022}^2 + 12v_{111}^2 - 2v_{022}b_{100}^2 + b_{100}^4) \right\}^2 \end{aligned} \quad (13)$$

For small $D/2k$, we get

$$J_{200} = \frac{3\sqrt{2}}{8} \frac{v_{111}^4}{k^2 b_{100}^2} \left(\frac{D}{2k} \right)^2 \left\{ 1 - \frac{1}{9} \left(\frac{D}{2k} \right)^2 (v_{022}^2 + 12v_{111}^2 - 2v_{022}b_{100}^2 + b_{100}^4) \right\}. \quad (14)$$

(13) and (14) represent the intensity of the 200-reflection averaged over the total solid angle corresponding to the rotation of the [200] direction of the crystal. The numerical factor 4 in the numerator of $4/4\pi k^2$ in (13) comes from the fact that there are four orientations giving rise to the 200-reflection through the double reflections among 111 , $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}1$ and $1\bar{1}\bar{1}$. According to the similar definition of the integrated intensity J_{200} given by (13), we can show the fact that the integrated intensity for the 222-reflection is equal to the half of J_{222} value given by (7). Therefore, the ratio of the integrated intensity of the 200-reflection to that of the 222-reflection for small $D/2k$ is given by

$$\frac{J_{200}}{J_{222}/2} = \frac{3\sqrt{2}}{8} \frac{v_{111}^4}{k^2 b_{100}^2} \left(\frac{D}{2k} \right)^2 / \frac{\sqrt{6}}{12} \frac{v_{111}^4}{k b_{111}} \left(\frac{D}{2k} \right)^3 = 3\sqrt{3} \frac{b_{111}}{b_{100}^2} \frac{1}{D}. \quad (15)$$

The ratio to the ordinary reflection such as the 111-reflection is given by

$$\frac{J_{200}}{J_{111}/2} = \frac{3\sqrt{6}}{32} \frac{v_{111}^2 b_{111}}{b_{100}^2} \frac{D}{k^2}. \quad (15')$$

In (15) and (15'), the multiplicity of reflection which is to be taken into account in the discussion of Debye patterns is not included. Introducing $b_{111}=1.94 \text{ \AA}^{-1}$ and $b_{100}=1.12 \text{ \AA}^{-1}$ into (15), we obtain

$$\frac{J_{200}}{J_{222}/2} = 8.04 \frac{1}{D} \quad (D: \text{A unit}). \quad (16)$$

This result shows that the ratio of the integrated intensity of the forbidden (200) arising from the accidental interactions to that of the forbidden (222) arising from the systematic interactions is independent of the wave length.

In the above calculation, we have considered the interactions among four waves 0, 200, 111 and $\bar{1}\bar{1}\bar{1}$ (Case I). It is interesting to compare the above result with that given by taking account of the interactions of three waves 0, 200 and 111 (Case II), since we can suppose that the latter approximation is better than the former for large ξ and $D/2k$, in view of the following circumstances. From (1-II), the intensity of the 200-reflection is given by

$$I_{200} = -2 \sum_{i,j} u_{200}^i u_{200}^j \sin^2 \left[\frac{D}{4k} (x^i - x^j) \right]. \quad (17)$$

As seen in Fig. 4(a), which shows a section of the dispersion surface at $\eta=0$ in Case I, $|x^i - x^j|$ ($i, j=1, 2, 3$) is appreciably larger than $|x^i - x^j|$ ($i, j=1, 2, 3$) at large ξ . As we have calculated the intensity by taking the terms in the power series expansion of $\sin^2[(D/4k)(x^i - x^j)]$ up to $(D/2k)^6$, and so long as such a terminated series is calculated, we are confronted with the frustrating increase in magnitude of the terms containing $|x^i - x^j|$ ($i=1, 2, 3$) with ξ , even if the corresponding $u_{200}^i u_{200}^j$ is small. Accordingly the calculated intensity decreases rapidly with ξ at large $D/2k$. In order to avoid such a apparent decrease, it is reasonable to assume Case II for the region of large ξ by neglecting the u_{200}^i i.e. not to take into account $\bar{1}\bar{1}\bar{1}$ -reciprocal lattice point. Fig. 4(b) shows the section of the dispersion surface at $\eta=0$ in such case.

The intensity formulas for $\eta=0$ are given, when $(\bar{1}\bar{1}\bar{1})$ is neglected, by

$$I_{200} = \frac{1}{4} \left(\frac{D}{2k} \right)^4 v_{111}^4 - \frac{1}{12} \left(\frac{D}{2k} \right)^6 v_{111}^6 - \frac{1}{9} \left(\frac{D}{2k} \right)^6 v_{111}^4 b_{100}^2 \left(\xi - \frac{\sqrt{2}}{4} b_{100} \right)^2, \quad (18)$$

and, when (111) is neglected, by

$$I_{200} = \frac{1}{4} \left(\frac{D}{2k} \right)^4 v_{111}^4 - \frac{1}{12} \left(\frac{D}{2k} \right)^6 v_{111}^6 - \frac{1}{9} \left(\frac{D}{2k} \right)^6 v_{111}^4 b_{100}^2 \left(\xi + \frac{\sqrt{2}}{4} b_{100} \right)^2, \quad (18')$$

where $\eta=0$ and $\xi = \sqrt{2}/4 \cdot b_{100}$ represents the position of the simultaneous reflection of 200- and 111-waves.

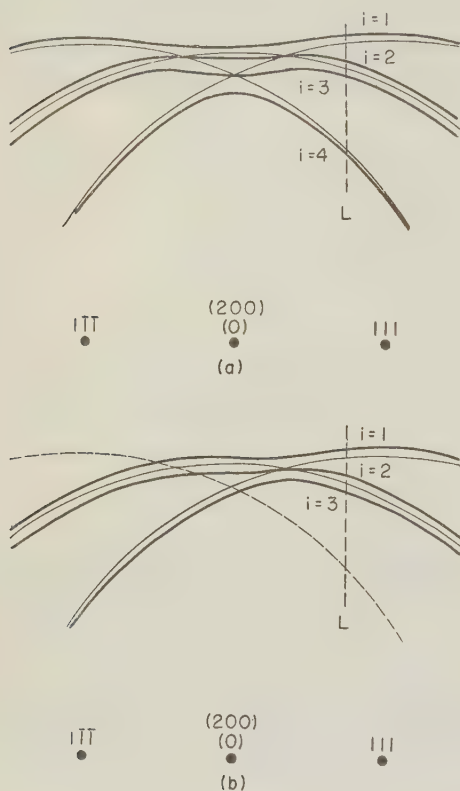


Fig. 4. Section of the dispersion surfaces for 200-reflection at $\eta=0$.

(a) Taking account of 0-, 200-, 111- and $11\bar{1}$ -waves.

(b) Taking account of 0-, 200- and 111-waves.

The intensities given by (12), (18) and (18') are shown by Curves 1, 2 and 2' in Fig. 5, respectively, in which (a) is for $D=50$ A and (b), for $D=100$ A ($k=100$ A⁻¹ in each case). In the case of $D=50$ A, Curve 1 is considered to give a better approximation for the range of small $|\xi|$ and Curves 2 and 2' for the range of large $|\xi|$. If we take into account a sufficient number of higher terms in (12), we may get the curve connecting Curve 1 with Curve 2 for $\xi > 0$ and with Curve 2' for $\xi < 0$, as shown schematically by the dotted curves in Fig. 5(a). As the integrated inten-

sity given by such a curve is mainly contributed by Curve 1, we may conclude that the exact value of J_{200} is approximated considerably well by (14). On the other hand, Fig. 5(b) indicates that the value of J_{200} calculated by (14) is too small compared with that due to the exact calculation, and suggests that it is necessary to take account of the higher terms in (12) in order to obtain J_{200} for thick crystals more exactly.

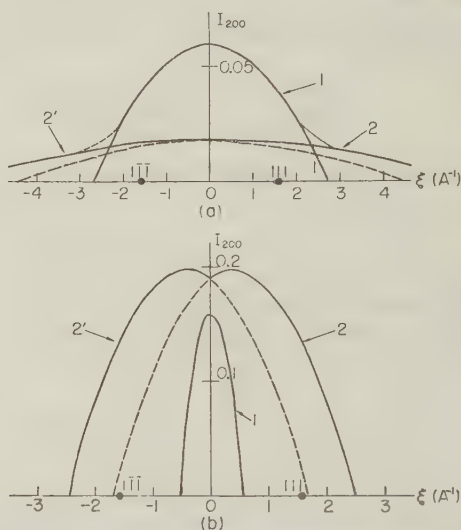


Fig. 5. Intensities of 200-reflection at $\eta=0$, $k=100$ A⁻¹.

(a) $D=50$ A and (b) $D=100$ A.

(1) Taking account of 0-, 200-, 111- and $11\bar{1}$ -waves.

(2) Taking account of 0-, 200- and 111-waves.

(2') Taking account of 0-, 200- and $11\bar{1}$ -waves.

§ 5. Discussions

i) In Fig. 1, we find that Curve 2, which corresponds to the intensity of the 222-reflection calculated by using the Mathieu function, nearly coincides up to fairly large thickness with Curve 3 given by the three-wave approximation taking account of 0, 111 and 222. This result indicates that the method of three-wave approximation, which is simpler than the method of the Mathieu function, is reliable for small $D/2k$.

However, we find appreciable difference between the intensity given by the Feynman expansion taking account of v_{333} , shown by Curve 1, and that shown by Curve 2. It is conceived that the intensity obtained by the Feynman expansion is more exact for small

$D/2k$. It diverges, however, at large $D/2k$, since we do not take into account the higher terms of the Feynman expansion, and the discrepancy between Curves 1 and 2 at large thickness seems to arise from this circumstance. More accurate calculation by the Feynman expansion is now being carried on, with the intention to compare its result with Curves 2 and 3 at the range of large $D/2k$.

ii) Since v_{222} of CuCl is vanishingly small, the intensity of this reflection can be dealt with by the present theory. The fact pointed out by Germer, that the intensity ratio of the 222-reflection to the 111-reflection in Debye patterns of CuCl is not proportional to the grain size, can be explained by the relation (9), according to which this ratio should be proportional to D^2 .

According to (7), (14) and (15), the dependence of the integrated intensity of the forbidden reflection (222) arising from the systematic interactions on D and k is different from that of the 200-reflection arising from the accidental interactions, and, in particular, the ratio of these integrated intensities is proportional to $1/D$ and independent of k for small $D/2k$. It is interesting to confirm these results by experiment.

Heidenreich³⁾ has explained the appearance of the 222-reflection of germanium by the accidental interactions between 311- and $\bar{1}11$ -reflections. So far as the intensity of Debye pattern is concerned, however, it is expected that the contribution of the accidental interactions is much smaller than that of the systematic interactions. According to (16), the thickness at which the integrated intensity

of the 222-reflection of germanium and that of the 200-reflection are comparable at about 8 Å. The forbidden reflection from such a thin crystal will be too weak to be observed. For thicker crystals, the intensity of the 222-reflection which is proportional to D^3 will be much stronger than that of the 200-reflection which is proportional to D^2 .

The 222-reflection in Debye patterns may contain the contributions both from the systematic and accidental interactions, but the former contribution will be dominant by the same reason as mentioned above.

Although, as clarified above, the integrated intensity J of reflections arising from accidental interactions may not be appreciable in most of cases, it should be noticed that the value of the intensity I of these reflection may be appreciable at its maximum.

The author would like to thank Prof. S. Takagi for his guidance and helpful discussions in this work.

References

- 1) H. Raether: *Z. Phys.* **78** (1932) 527.
- 2) L. H. Germer: *Phys. Rev.* **56** (1939) 58; **61** (1942) 309.
- 3) R. D. Heidenreich: *Phys. Rev.* **77** (1950) 271.
- 4) J. A. Hoerni: *Phys. Rev.* **102** (1956) 1534.
- 5) M. Takagi and S. Morimoto: private communication.
- 6) F. Fujimoto: *J. Phys. Soc. Japan* **14** (1959) 1558; **15** (1960) 859.
- 7) *Tables Relating to Mathieu Functions*, U. S. Nat. Bur. Stand. (Columbia Univ. Press, New York, 1951).
- 8) J. A. Ibers: *Acta Cryst.* **11** (1958) 178.
- 9) M. Blackman: *Proc. Roy. Soc. A*, **173** (1939) 68.

Study on the Ordered Alloys of Gold-Manganese System by Electron Diffraction, I. Au_3Mn^*

By Denjiro WATANABE

*The Research Institute for Iron, Steel and Other Metals,
Tohoku University, Sendai, Japan*

(Received February 5, 1960)

The ordered structure of Au_3Mn alloy has been investigated by electron diffraction using oriented, evaporated films. The structure can be thought of as formed from the fundamental face-centred orthorhombic lattice, in which the atoms arrange themselves as in the ordered lattice of Cu_3Au but the first kind of out-of-step periodically occurs along both the x and y directions. In some cases the periods are $1.2 a_1$ and $2.2 a_2$ respectively, where $a_1=4.08\text{\AA}$, $a_2=4.05\text{\AA}$, $a_3=4.03\text{\AA}$ are the lattice constants of the fundamental lattice. Thus, a two-dimensional anti-phase domain structure of a new type takes place, which belongs to the space group $P_{nm}\cdot D_{2h}^{12}$ in the idealized case.

§ 1. Introduction

Recently, the gold-manganese alloy system was investigated by Raub, Zwicker and Baur¹⁾ and Kussmann and Raub²⁾, and the phase diagram as shown in Fig. 1 was proposed. According to them, two types of ordered alloy, Au_3Mn and Au_4Mn , are present in the α phase which is face-centred cubic in the disordered state. The former alloy has an ordered structure with tetragonal symmetry below about 645°C and the latter alloy has an ordered face-centred tetragonal lattice ($c/a < 1$) below about 420°C , but the atomic arrangement in both phases has as yet been unknown. On the other hand, it was shown by Kussmann and Raub²⁾ and Meyer^{3), 4)} that these ordered alloys have interesting magnetic properties. That is to say, the ordered Au_4Mn is ferromagnetic below about 88°C , and the ordered Au_3Mn is metamagnetic like Au_2Mn ⁵⁾, having the Néel point of antiferromagnetism at about 145°K , while the disordered cubic Au_3Mn phase quenched from above 625°C is ferromagnetic below 120°K . It is natural that these magnetic properties are closely connected with the crystal structures of both phases, but a full explanation of the above properties has not been given due to a lack of information on the crystal structure. Thus, the present electron diffraction work has been undertaken to elucidate the complex crystal structure of the ordered

alloys, Au_3Mn and Au_4Mn , using single-crystalline evaporated thin films.

In the present paper, it will be shown that the ordered structure of Au_3Mn is formed from the fundamental face-centred orthorhombic lattice in which the atoms arrange themselves as in the ordered structure of Cu_3Au , and that the first kind of out-of-step periodically occurs along both the x and y directions and therefore a two-dimensional anti-phase domain structure of a new type is formed.

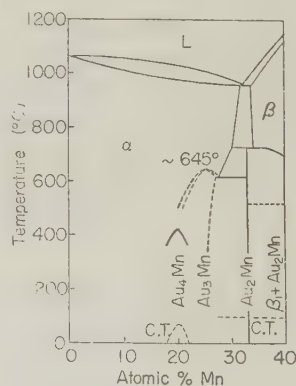


Fig. 1. Gold-rich side of the phase diagram of gold-manganese system.

The satellites flanking main reflections were observed also in the present alloy, the circumstances being the same as in CuAu(II) ⁶⁾ and Cu_3Pd ⁷⁾. Discussion on the origin of the satellites will be given in Part III⁸⁾ of the present work. The result concerning the ordered alloy Au_4Mn will be reported in Part II⁹⁾.

* A short note concerning this work has been published in J. Phys. Soc. Japan **13** (1958) 535.

§ 2. Experimental Method

Single-crystalline films of gold-manganese alloys were prepared in the following way: oriented gold films were first formed *in vacuo* on cleavage surfaces of rocksalt heated at 400°C, and secondly, after the films were detached from the substrates in water, mounted on nickel supporters and heated at 450~500°C, manganese was evaporated *in vacuo* on them. The composite films were immediately annealed without breaking vacuum at about 450°C for 1~2 hr., in order to bring about the alloying and to avoid the oxidation of manganese. A gold wire drawn into 0.19 mm in diameter and a plate of electrolytic manganese 1 mm in thickness were used as materials to be evaporated. Both metals had a purity of 99.99 per cent. The thickness of the alloy films estimated from the evaporated quantities was 400~450Å.

Films formed as above were heated *in vacuo* in a silica tube and quenched by pouring water onto the tube, and all the diffraction patterns were obtained from quenched films. The heat-treatment was carried out in the temperature range between 300 and 700°C for various durations, but the treatment above 600°C was stopped within 0.5~1 hr., because there was the possibility of oxidation of manganese and of the change of film composition in the course of a long period of heating. The Au₃Mn phase films quenched from 700°C showed superlattice reflections which Raub *et al.*¹¹ also obtained from quenched specimens, because the quenching of the disorder state was not successful owing to very quick formation of the ordered phase. Hence, the investigation concerning the disordered state of the Au₃Mn phase was not carried out, and therefore the lattice constant of the disordered face-centred cubic lattices was not measured in the present work. Even if it were possible, however, the atomic composition of alloy films could not be determined from the lattice constant of the cubic phase as usual, because a change of lattice constants of this phase with the manganese content is very small (4.06~4.05Å), as reported by Bumm and Dehlinger.¹⁰ The composition was estimated both from the quantities of metals evaporated and from comparison of the observed alloy structure with the X-ray results previously reported.^{1), 2)}

A diffraction camera of a camera length 309 mm made by the Hitachi Co. was used, the applied voltage being about 50 kV. Although the intensities of diffraction spots were estimated visually in most of the photographic plates, a microphotometer was used in some cases in order to compare the intensities calculated from the proposed structure model with the observed ones. As pointed out by Cowley,¹¹ the microphotometer method is difficult to measure the intensity of the focused spots photographically recorded, but the present author adopted tentatively the following procedure: A series of diffraction photographs of one and the same specimen was successively taken with different exposures, and the photometry was performed. Intensity distribution curves were obtained from microphotometer traces, utilizing Karle and Karle's method.¹² Integrated intensities of the diffraction spots were evaluated by measuring the peak area of the intensity curve. The intensities of very weak spots of higher order, however, were visually estimated.

§ 3. Superstructure of Au₃Mn

(1) Electron diffraction pattern

Films containing about 25 per cent manganese,* which were annealed at 450°C for 1 hr. after the deposition of manganese and were slowly cooled down to room temperature with cooling velocity of 5°C/min., already exhibited complex superlattice reflections, besides main reflections. The patterns did not change their aspects even after the films were annealed at 700°C for 0.5~1 hr. and slowly cooled down to room temperature, and therefore it was considered that the alloying, and also the ordering, were sufficiently accomplished by the annealing at 450°C for 1 hr. after the deposition. In order to attain the complete ordering, however, further heat-treatments were carried out mainly below 500°C.

Details of the aspects of diffraction patterns will be described as follows: Photo. 1 shows a typical pattern of a thin alloy film containing about 25 per cent manganese, which was slowly cooled after annealing at 450°C for 2 hr. It was found from the splits of the

* In the present paper, all percentages refer to atomic per cent.

main reflections that the fundamental lattice of the ordered Au_3Mn is face-centred orthorhombic close to cubic, the lattice constants being $a_1 = 4.08$, $a_2 = 4.05$, $a_3 = 4.03 \pm 0.01 \text{ \AA}$, while Raub and others¹⁾ reported that this phase has a fundamental cell of face-centred tetragonal, the axial ratio being close to unity. Although the pattern in Photo. 1 resembles to some extent that of the ordered alloy Cu_3Pd ,⁷⁾ the split manner of superlattice reflections is more complex. Satellites are also observed around the main reflections as in CuAu (II) and Cu_3Pd . An illustration of Photo. 1 is shown in Fig. 2, where superlattice reflections and satellites are represented by the small closed and open circles respectively. Mutual distances of the superlattice reflections in each group and separations of

satellites from each relevant main reflection are defined by two values of separation, " m_1 " and " m_2 ". Aspects of patterns change very little with a slight change of the composition, but the ratios of m_1 and m_2 to the fundamental reciprocal lattice constants were found to change to some extent. On the analogy of anti-phase domains in CuAu (II) and Cu_3Pd , therefore, the complex superlattice reflections may be considered to be formed by splits of reciprocal points with indices of mixed integers.

Such a complex pattern as above scarcely changed after a prolonged annealing below the critical point of order-disorder (T_c),* and the lattice spacings measured from main reflections and superlattice reflections almost coincided with those obtained from an X-ray Debye photograph of the Au_3Mn alloy by Raub and others,¹⁾ as shown in the third and the fourth column of Table I, so that diffraction pattern as shown in Photo. 1 was confirmed to reveal the ordered state of the Au_3Mn alloy.

(2) Interpretation for the diffraction pattern and determination of the structure

As described in the preceding section, the patterns obtained from the ordered Au_3Mn resemble those of the ordered alloys with anti-phase domains, CuAu (II) and Cu_3Pd , in the splitting of superlattice reflections and in the appearance of satellite spots flanking the intense main reflections, but the present split manner differs from either case. The fact that the fundamental lattice of the present alloy is orthorhombic, as mentioned above, is readily found both from the fine splits of main reflections of higher indices and from the positions of split superlattice reflections in Photo. 1 and Fig. 2. The fine splits of main reflections mean that the pattern corresponds to a superposition of several orientations, as was the case with Cu_3Au , CuAu (II) and Cu_3Pd . After a careful examination the fundamental intensity distribution in reciprocal space, corresponding to one orientation, can be derived, as shown in Fig. 3, where the indices, $(h_1h_2h_3)$, are used in terms of the fundamental lattice. The actual intensi-

Photo. 1. Electron diffraction pattern of the ordered Au_3Mn film; normal incidence. Indices assigned to normal reflections refer to the disordered cubic lattice.

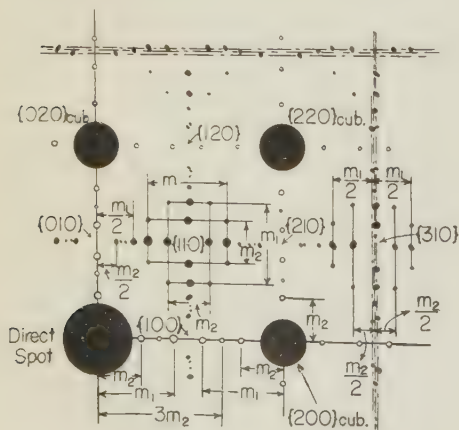


Fig. 2. Illustration of Photo. 1.

* In alloy films containing manganese less than 25 per cent, the pattern changed after annealing at temperatures below 400°C , as will be reported in Part II.

Table I. Lattice spacings of the ordered Au_3Mn .

h_1	h_2	h_3^*	$d_{cal}(\text{\AA})$ $M_1=1.2$ $M_2=2.2$	$d_{obs.}(\text{\AA})$	$d_{x-ray}(\text{\AA})^{**}$	$d_{cal}(\text{\AA})$ $M_1=1.0$ $M_2=2.2$	h_1	h_2	h_3^*
(0, ±1/2M ₂ , 0)			8.91	9.15		8.91	(0, ±1/2M ₂ , 0)		
(±1/2M ₁ , 0, 0)			4.89	4.81		4.41	(1-1/2M ₁ , 1-1/2M ₂ , 0)		
1-1/2M ₁ , 1-1/2M ₂ , 0			4.193	4.21		4.080	(±1/2M ₁ , 0, 0)		
1, ±1/2M ₂ , 0			3.976	3.99		3.976	1, ±1/2M ₂ , 0		
±1/2M ₁ , 1, 0			3.742	3.74					
±1/2M ₁ , 0, 1			3.726						
±1/2M ₁ , ±1/2M ₂ , 1			3.647	3.63		3.627	±1/2M ₁ , 1, 0		
(2-1/2M ₁ , 0, 0)			3.498	3.54		3.614	±1/2M ₁ , 0, 1		
1-1/2M ₁ , 1, 0			3.504	3.51					
1-1/2M ₁ , 0, 1			3.491						
0, 1-1/2M ₂ , 1			3.195	3.20		3.195	0, 1-1/2M ₂ , 1		
1-1/2M ₁ , 1+1/2M ₂ , 0			2.984	3.01		3.059	1-1/2M ₁ , 1+1/2M ₂ , 0		
(0, 2-1/2M ₂ , 0)			2.620	2.61		2.620	(0, 2-1/2M ₂ , 0)		
0, 1+1/2M ₂ , 1			2.553	2.57	2.556 v.v.w.	2.553	0, 1+1/2M ₂ , 1		
1+1/2M ₁ , 1-1/2M ₂ , 0			2.523	2.52	2.423 v.w.	2.414	1+1/2M ₁ , 1-1/2M ₂ , 0		
1+1/2M ₁ , 1, 0			2.347	2.35					
1+1/2M ₁ , 0, 1			2.343						
1, 1, 1			2.340	2.34	2.314 m.st.	2.340	1, 1, 1		
2-1/2M ₁ , 1, 0			2.174	2.19		{2.258	1+1/2M ₁ , 1, 0		
2-1/2M ₁ , 0, 1			2.172		2.258 v.w.	{2.254	1+1/2M ₁ , 0, 1		
1+1/2M ₁ , 1+1/2M ₂ , 0			2.169	2.18	2.216 v.w.	2.237	2-1/2M ₁ , ±1/2M ₂ , 1		
2-1/2M ₁ , ±1/2M ₂ , 1			2.155	2.16	2.116 w.	2.099	1+1/2M ₁ , 1+1/2M ₂ , 0		
2, 0, 0			2.040	2.040	2.088 v.w.	2.040	2, 0, 0		
0, 2, 0			2.025	2.023		2.025	0, 2, 0		
0, 0, 2			2.015	2.016		2.015	0, 0, 2		
1, 2-1/2M ₂ , 0			1.993	1.994		{1.993	1, 2-1/2M ₂ , 0		
(2, ±1/2M ₂ , 0)			1.988	1.970	2.000 v.v.w.	{1.988	(2, ±1/2M ₂ , 0)		
±1/2M ₁ , 2-1/2M ₂ , 1			1.947	1.947		{1.930	±1/2M ₁ , 2-1/2M ₂ , 1		
(±1/2M ₁ , 2, 0)			1.871	1.864	1.875 v.w.	{1.833	1-1/2M ₁ , 1-1/2M ₂ , 2		
1-1/2M ₁ , 1-1/2M ₂ , 2			1.817	1.820		{1.813	(±1/2M ₁ , 2, 0)		
1, ±1/2M ₂ , 2			1.797	1.799	1.799 v.w.	{1.797	1, ±1/2M ₂ , 2		
±1/2M ₁ , 2, 1			1.780	1.774		{1.766	±1/2M ₁ , 2, 1		
±1/2M ₁ , 1, 2			1.774			{1.761	±1/2M ₁ , 1, 2		
(2-1/2M ₁ , 2, 0)			1.752	1.754					
1-1/2M ₁ , 2, 1			1.751	1.762					
1-1/2M ₁ , 1, 2			1.747						
2, 1-1/2M ₂ , 1			1.719	1.716					
1-1/2M ₁ , 1+1/2M ₂ , 2			1.670	1.680		1.683	1-1/2M ₁ , 1+1/2M ₂ , 2		
1, 2+1/2M ₂ , 0			1.661	1.671		1.661	1, 2+1/2M ₂ , 0		
(0, 2+1/2M ₂ , 0)			1.650	1.659		1.650	(0, 2+1/2M ₂ , 0)		
±1/2M ₁ , 2+1/2M ₂ , 1			1.634	1.646		1.624	±1/2M ₁ , 2+1/2M ₂ , 1		
(2, 2-1/2M ₂ , 0)			1.610	1.599	1.606 v.v.w.	{1.610	(2, 2-1/2M ₂ , 0)		
2, 1+1/2M ₂ , 1			1.593	1.601		{1.604	2-1/2M ₁ , 2-1/2M ₂ , 1		
1+1/2M ₁ , 1-1/2M ₂ , 2			1.575	1.574		{1.593	2, 1+1/2M ₂ , 1		
2-1/2M ₁ , 2-1/2M ₂ , 1			1.573	1.583	1.576 v.v.w.	{1.558	3-1/2M ₁ , 1-1/2M ₂ , 0		
2+1/2M ₁ , 1, 0			1.558	1.559		{1.554	2, 1-1/2M ₂ , 1		
2+1/2M ₁ , 0, 1			1.557			{1.547	1+1/2M ₁ , 1-1/2M ₂ , 2		
1+1/2M ₁ , 2, 1			1.532	1.533					
1+1/2M ₁ , 1, 2			1.529			{1.514	2+1/2M ₁ , 1, 0		
3-1/2M ₁ , 1-1/2M ₂ , 0			1.512	1.518	1.524 v.v.w.	{1.513	2+1/2M ₁ , 0, 1		
2-1/2M ₁ , 2, 1			1.481	1.482	1.497 v.w.	{1.506	1+1/2M ₁ , 2, 1		
2-1/2M ₁ , 1, 2			1.478			{1.503	1+1/2M ₁ , 1, 2		
3-1/2M ₁ , 0, 1			1.471	1.478					
2, 2, 0			1.437	1.437		1.438	1-1/2M ₁ , 3-1/2M ₂ , 0		
2, 0, 2			1.434	1.434		{1.437	2, 2, 0		
1-1/2M ₁ , 3-1/2M ₂ , 0			1.430	1.430	1.423 m.st.	{1.434	2, 0, 2		
0, 2, 2			1.428	1.428		{1.428	0, 2, 2		
1, 2-1/2M ₂ , 2			1.417	1.416		{1.417	1, 2-1/2M ₂ , 2		
0, 3-1/2M ₂ , 1			1.373	1.380	1.378 v.w.	1.373	0, 3-1/2M ₂ , 1		
3, ±1/2M ₂ , 0			1.356	1.356	1.350 w.	1.356	3, ±1/2M ₂ , 0		
±1/2M ₁ , 3, 0			1.337	1.339					
±1/2M ₁ , 0, 3			1.331	1.332		1.332	±1/2M ₁ , 3, 0		
±1/2M ₁ , ±1/2M ₂ , 3			1.327			1.326	±1/2M ₁ , 0, 3		
1-1/2M ₁ , 0, 3			1.319	1.321	1.314 v.v.w.	1.322	±1/2M ₁ , ±1/2M ₂ , 3		
1-1/2M ₁ , 3-1/2M ₂ , 0			1.302	1.303		{1.301	0, 1-1/2M ₂ , 3		
0, 1-1/2M ₂ , 3			1.301	1.302	1.292 v.w.	{1.287	1+1/2M ₁ , 3-1/2M ₂ , 0		
1, 2+1/2M ₂ , 2			1.282	1.288	1.260 v.v.w.	1.282	1, 2+1/2M ₂ , 2		
0, 1+1/2M ₂ , 3			1.244	1.248		1.244	0, 1+1/2M ₂ , 3		

Table I. (Continued)

h_1	h_2	h_3^*	$d_{\text{cal}}(\text{\AA})$ $M_1=1.2$ $M_2=2.2$	$d_{\text{obs.}}(\text{\AA})$	$d_{x\text{-ray}}(\text{\AA})^{**}$	$d_{\text{cal}}(\text{\AA})$ $M_1=1.0$ $M_2=2.2$	h_1	h_2	h_3^*
$2+1/2M_1$,	2,1		1.234{	1.238	1.216 st.	1.228	3,		1,1
$2-1/2M_1$,	1,2		1.233{			1.221	1,		3,1
3,	1,1		1.228			1.217	1,		1,3
1,	3,1		1.221			1.212	$2+1/2M_1$,		2,1
1,	1,3		1.217	1.220		1.210	$2+1/2M_1$,		1,2
$1+1/2M_1$,	0,3		1.217	1.218		1.209	$2-1/2M_1$,		3,0
0, $3+1/2M_2$,	1		1.198	1.204	1.203 v.v.w.	1.204	$1+1/2M_1$,		0,3
$2-1/2M_1$,	3,0		1.196	1.199	1.191 v.v.w.	1.198	0, $3+1/2M_2$,		1

* Parenthesized indices, $(h_1h_2h_3)$, correspond to satellites flanking the main reflections.

** Lattice spacings measured by Raub and others were obtained from an alloy containing 26.5 per cent manganese.

ty distribution in Photo. 1 and Fig. 2 corresponds to a sixfold superposition of that of Fig. 3.

Now, we shall examine the intensity distribution on the basis of anti-phase domains. As readily supposed from Fig. 3, all the superlattice reflections are thought of as formed by the splitting of the reciprocal lattice points with mixed integers, h_1h_2 and h_3 , the distances of splitting being $\pm m_1/2$ along the $[h_100]$ direction and $\pm m_2/2$ along the $[0h_20]$ direction respectively. Hence, it is probable that the ordered lattice of Au_3Mn is built up from face-centred orthorhombic cells with the atomic arrangement similar to that in Cu_3Au but possesses two kinds of out-of-steps along the a_1 and a_2 directions. According to the concept of anti-phase domain structure,^{(6),(7)} the splits of the superlattice reflections with mixed h_2 and h_3 along the $[h_100]$ direction

and of those with mixed h_1 and h_3 along the $[0h_20]$ direction suggest that there are line-ups of anti-phase domains with stepshifts, $\pm(a_2\pm a_3)/2$ and $\pm(a_3\pm a_1)/2$, at every M_1 cells and at every M_2 cells along the x and y directions respectively. Here a_1 , a_2 and a_3 are the fundamental lattice vectors along the x , y and z axes. It should be noted from the split manner of superlattice reflections, especially from the double splits of (110) in Fig. 3, that these two kinds of out-of-steps do not occur independently but are intimately connected with each other in a crystal, forming a two-dimensional anti-phase domain structure, as was the case with Cu_3Pd . In reciprocal space the separation of the split superlattice spots measured from the centre of the splitting† is given by $n_1a_1^*/2M_1$ or $n_2a_2^*/2M_2$ which satisfies the following relation,

$$m_1/2 = a_1^*/2M_1 \text{ or } m_2/2 = a_2^*/2M_2, \quad (1)$$

where a_1^* and a_2^* are reciprocal lattice constants corresponding to a_1 and a_2 respectively and n_1 and n_2 are odd integers. A model of the crystal structure of the ordered Au_3Mn derived from the above consideration is proposed, as shown in Fig. 4. M_1 and M_2 were measured from separations of split superlattice reflections, using Eq. (1), and were found to have fractional values slightly larger than 1 and 2 respectively. However, they are assumed to be 1 and 2 in Fig. 4. That is to say, we deal with an idealized case in the present model. If these M 's were definite throughout the crystal, a large orthorhombic cell shown by the broad black lines

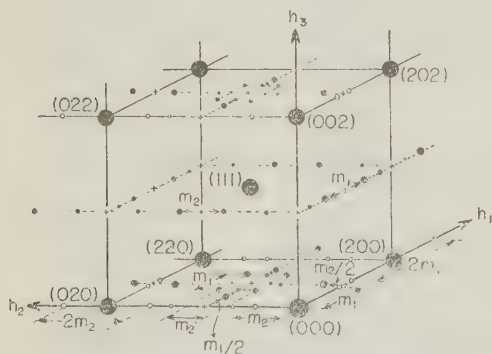


Fig. 3. Fundamental intensity distribution in reciprocal space derived from diffraction patterns of Au_3Mn film. Superlattice reflections and satellites are represented by the small closed and open circles respectively. The cross represents the centre of the splitting of the superlattice reflections.

† The centre of the splitting corresponds to the reciprocal lattice point with mixed integers, h_1h_2 and h_3 , and is represented by the cross in Fig. 3.

would be considered to be the unit cell of this ordered alloy.

Some explanations seem to be required about this model. When the large unit cell is divided into four domains, as shown by the broken lines, it can readily be seen that each domain is built up from face-centred cells with the atomic arrangement similar to that in Cu_3Au and that the sites of manganese atoms in four domains correspond to four basic sites in the face-centred lattice,

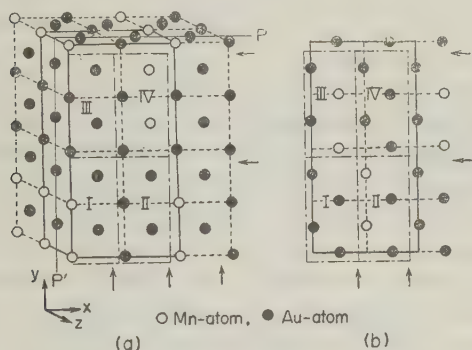


Fig. 4. A model of the two-dimensional anti-phase domain structure of Au_3Mn . $M_1=1$ and $M_2=2$ are chosen in this model. Out-of-steps occur at places indicated by arrows.

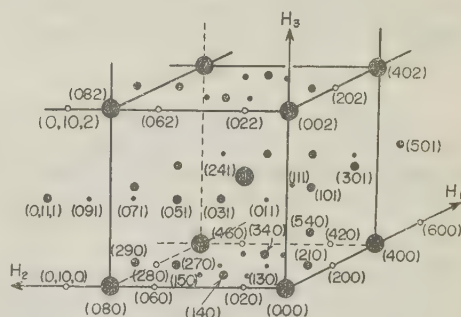
(a) Large orthorhombic unit cell is shown by the broad black lines.

(b) Distribution of atoms in the plane PP' situated immediately behind the front plane in (a).

respectively. Moreover, it will be seen that the domains III and IV can be built up by the introduction of the shifts, $\pm(a_3 \pm a_1)/2$, at every M_2 cells along the y direction into the domains I and II, respectively, and also the domains II and IV can be built up by the introduction of the shifts, $\pm(a_2 \pm a_3)/2$, at every M_1 cells along the x direction into the domains I and III, respectively. Here, the stepshifts both belong to "the first kind" and therefore the present two-dimensional structure is different from that found in Cu_3Pd . If the domains II and IV change places with each other, a Cu_3Pd type anti-phase domain structure is built up.

Now, we shall re-examine the crystal structure of the present alloy from a viewpoint of the conventional structure analysis based on the space group. For this purpose, all the reflections in reciprocal space in Fig. 3 should be indexed with integers. As already

mentioned, however, M 's are actually fractional numbers, and therefore, all the reflections should be given indices with large number and hence an enormous unit cell would have to be assumed. This makes an analysis fairly difficult, and more over, it may be somewhat waste of labor, because M 's vary with composition. Therefore, we simplified the problem, starting afresh by assuming M 's to be integers nearest to their true values. This procedure made the indices simpler, and hence the unit cell became smaller. Fig. 5 shows the reciprocal lattice obtained in this way,* which corresponds to an orthorhombic unit cell $2 \times 4 \times 1$ times as large as the fundamental cell. Though this idealization displaces superlattice reflections and satellites from their true positions, it is clear that the general character of the problem is not altered, as will be described later.



able to explain the intensity distribution in Fig. 5 best. It can easily be seen that the atomic arrangement in this figure is identical with that obtained in Fig. 4. That is to say, the fundamental lattice has an atomic arrangement similar to Cu₃Au and the first kind of out-of-steps occurs at every cell of

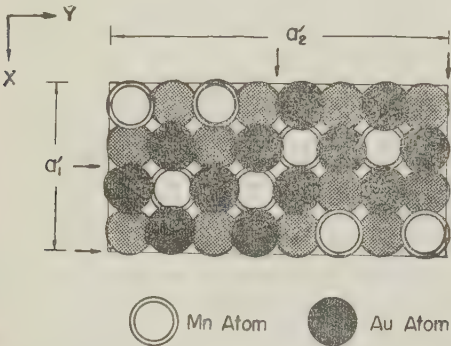


Fig. 6. The ordered structure of Au₃Mn, viewed along [001]_{cub}. Out-of-steps occur at places indicated by arrows. $a_1'=2a_1=8.16\text{\AA}$, $a_2'=4a_2=16.20\text{\AA}$.

the fundamental lattice along the x direction and also at every two cells along the y direction.

The structure amplitude for the lattice shown in Fig. 6, F , is given by the following equation.

$$F=4\sum_{i=1}^8E_i\cdot\cos2\pi H_1x_i\cdot\cos2\pi H_2y_i$$

for $H_1+H_2+H_3=2n$,

$$F=-4\sum_{i=1}^8E_i\cdot\sin2\pi H_1x_i\cdot\sin2\pi H_2y_i$$

for $H_1+H_2+H_3=2n+1$,

(2)

where E_i is the atomic scattering factor for electron of i -th atom. In Table II, $|F_{\text{cal}}|$ of reflections with $(H_1\ H_2\ 0)$ indices calculated from the above equation is tabulated. Fig. 7 shows the intensity distribution in reciprocal space corresponding to the proposed model. As already mentioned, the intensity distribution in reciprocal space corresponding to an actual ordered alloy must be a sixfold super-

Table II. The observed and calculated structure amplitudes for the ordered Au₃Mn.

H_1, H_2, H_3	$ F_{\text{obs}} $	$ F_{\text{cal}} $	H_1, H_2, H_3	$ F_{\text{obs}} $	$ F_{\text{cal}} $	H_1, H_2, H_3	$ F_{\text{obs}} $	$ F_{\text{cal}} $
4, 0, 0	212	195	1, 3, 0	16	18	5, 12, 0	13	12
8, 0, 0	92	92	3, 3, 0	14	15	7, 12, 0	10	10
12, 0, 0	55	53	5, 3, 0	11	11	9, 12, 0	8	8
4, 8, 0	130	138	7, 3, 0	8	9	11, 12, 0	6	6
8, 8, 0	74	79	9, 3, 0	6	6	1, 20, 0	9	9
12, 8, 0	46	48	11, 3, 0	5	5	3, 20, 0	9	8
4, 16, 0	74	79	1, 5, 0	15	17	5, 20, 0	7	8
8, 16, 0	49	58	3, 5, 0	14	14	7, 20, 0	7	7
4, 24, 0	46	48	5, 5, 0	10	11	Satellites		
8, 24, 0	24	38	7, 5, 0	8	8	2, 0, 0	17	0
0, 8, 0	212	194	9, 5, 0	6	6	6, 0, 0	11	0
0, 16, 0	92	91	11, 5, 0	5	5	10, 0, 0	7	0
0, 24, 0	55	52	1, 11, 0	10	10	2, 8, 0	14	0
Superlattice reflections			3, 11, 0	10	9	6, 8, 0	8	0
2, 1, 0	24	26	5, 11, 0	8	8	6, 8, 0	8	0
6, 1, 0	13	14	7, 11, 0	7	7	10, 8, 0	5	0
10, 1, 0	9	8	9, 11, 0	5	5	2, 16, 0	7	0
2, 3, 0	7	10	1, 13, 0	9	9	6, 16, 0	5	0
6, 3, 0	4	6	3, 13, 0	10	9	10, 16, 0	4	0
2, 5, 0	5	9	5, 13, 0	8	7	2, 24, 0	5	0
2, 7, 0	20	19	7, 13, 0	6	6	0, 24, 0	17	0
6, 7, 0	12	13	9, 13, 0	5	5	0, 6, 0	12	0
10, 7, 0	7	8	1, 19, 0	6	6	0, 10, 0	10	0
2, 9, 0	19	16	3, 19, 0	5	6	0, 14, 0	7	0
6, 9, 0	12	12	5, 19, 0	5	5	0, 18, 0	3	0
10, 9, 0	8	7	1, 21, 0	5	5	4, 2, 0	10	0
2, 11, 0	4	6	3, 21, 0	5	5	4, 6, 0	8	0
2, 15, 0	12	11	1, 4, 0	25	27	4, 10, 0	7	0
6, 15, 0	9	8	3, 4, 0	21	23	4, 14, 0	5	0
10, 15, 0	4	6	5, 4, 0	16	16	4, 18, 0	3	0
2, 17, 0	10	9	7, 4, 0	14	13	8, 2, 0	6	0
6, 17, 0	7	8	9, 4, 0	11	10	8, 6, 0	5	0
2, 23, 0	6	6	11, 4, 0	8	8	8, 10, 0	5	0
2, 25, 0	6	6	13, 4, 0	4	6	8, 14, 0	3	0
			1, 12, 0	15	15	12, 2, 0	4	0
			3, 12, 0	14	14	12, 6, 0	3	0

position of the intensity distribution in Fig. 7. The coincidence of Fig. 7 with Fig. 5 is very good, concerning the splits of the superlattice reflections. Therefore, it seems that the present model almost represents the ordered structure of this alloy. However, there are some disagreements between the model and the observed facts as follows:

(i) Those satellites flanking intense main reflections, which are represented by small open circles in Figs. 3 and 5, cannot be derived from the present model. The circumstance is the same as in CuAu (II) and Cu_3Pd . It is sure that the satellites arise from the lattice modulation, such as a periodic change of the lattice spacing or of the scattering factor, with the same period as that of out-of-steps. The detailed discussion will be given in Part III.

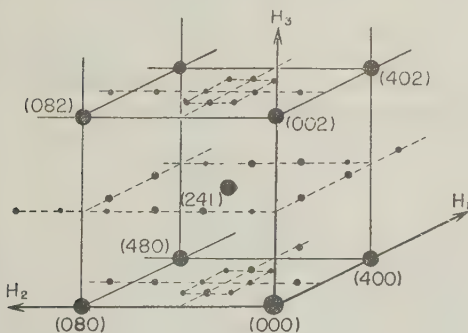


Fig. 7. Fundamental intensity distribution in reciprocal space derived from the proposed model.

(ii) Strictly speaking, the positions of the split superlattice reflections in Fig. 3 do not coincide with those in Figs. 5 and 7. This disagreement is attributable to the fact that M_1 and M_2 are not 1 and 2, as assumed in the analysis, but fractional values. The measured values of M_1 and M_2 change from 1.0 and 2.1 to 1.3 and 2.5 respectively with the alloy composition and the heat-treatment.* According to Fujiwara,¹³⁾ the fractional property of domain size means a mixture of different sizes of domains in the actual lattice. Thus, an enormous unit cell has to be taken as an exact unit cell for the actual, fractional domain size. For example, if we start from Fig. 3, where M_1 and M_2 are measured to be

about 1.2 and 2.2 respectively† and the extinction rule is the same as in Fig. 5, we are able to deduce the positions of gold and manganese atoms on the basis of the same space group as above, $Pnmm-D_{2h}^{12}$, taking into account a large orthorhombic cell with the size of $12a_1 \times 22a_2 \times a_3$, but the atomic arrangement obtained in this way is nothing but the two-dimensional anti-phase domain structure in which domains with $M_1=2$ and $M_2=3$ are uniformly mixed in domains with $M_1=1$ and $M_2=2$ along the x and y directions respectively. Of course, different modes of

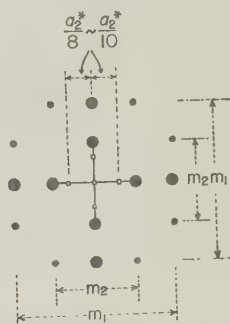


Fig. 8. Detailed illustration of splits in $\{110\}_{cub.}$. The weak streaks and the excessive peaks are shown by the straight lines and the open squares respectively.

mixture of domains are conceivable, because a uniform irregular mixture and a uniform regular mixture of different sizes of anti-phase domains yield a similar intensity distribution of diffraction, as pointed out by Fujiwara. It should be noted that after a careful examination of the patterns of the present alloy we can often observe very weak streaks connecting a pair of split superlattice reflections and excessive peaks with weak intensities on the streaks, as shown in Fig. 8, where the streaks and the excessive peaks are illustrated by the straight lines and the open squares respectively. The separations of the excessive peaks from the centre of splits are approximately zero and $\pm a_2^*/8 \sim a_2^*/10$ and correspond to $\pm ka_2^*/2\nu M_2$ with $k=0$ and integer, where $2\nu M_2$ (ν : positive integer) is a minimum value of integer.†† This

† Exactly speaking, M_1 and M_2 are 1.18 and 2.24, respectively.

†† If M_2 is 2.24, $2\nu M_2$ is 112. k -values corresponding to the excessive peaks are approximately zero and 14~11.

* The estimated error of the M value is ± 1 per cent.

fact is well explained by the theory of Fujiwara and of Perio and Tournarie.¹⁴⁾ The latter investigators also treated mathematically the problem of the fractional property of the size of domains. The present case seems to correspond to the irregular statistical arrangement with a certain degree of non-uniform mixing in the treatment of Fujiwara.

At any rate, it is obvious that the ordered structure of the present alloy is the two-dimensional anti-phase domain structure with the first kind of out-of-steps, and the model shown in Figs. 4 and 6 reveals an idealized lattice. In Table I, the lattice spacings measured from diffraction spots in Photo. 1 are compared with the spacings calculated from the model with $M_1=1.2$ and $M_2=2.2$, and the fairly good coincidence is seen except the satellites. On the other hand, the spacings obtained by Raub *et al.*¹⁾ are almost explained by the model with $M_1=1.0$ and $M_2=2.2$.

(3) Comparison between observed and calculated structure amplitudes.

Next, the structure amplitude obtained from the observed intensity, $|F_{\text{obs}}|$, will be compared with $|F_{\text{cal}}|$ calculated from equation (2). Integrated intensities of the diffraction spots were measured photometrically as well as visually, as mentioned in §2, taking into account the fact that the diffraction pattern as shown in Photo. 1 reveals a superposition of the intensity distributions in the three planes of coordinates, (H_1H_20) , $(0H_2H_3)$ and (H_10H_3) , in reciprocal space.

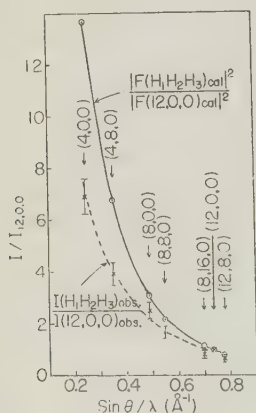


Fig. 9. Comparison of $I(H_1H_2H_3)_{\text{obs}}/I(12,0,0)_{\text{obs}}$ and $|F(H_1H_2H_3)_{\text{cal}}|^2/|F(12,0,0)_{\text{cal}}|^2$.

In the kinematical theory the integrated intensity is given by

$$I(H_1H_2H_3) \propto |F(H_1H_2H_3)|^2. \quad (3)$$

$I(H_1H_2H_3)_{\text{obs}}/I(12,0,0)_{\text{obs}}$ and $|F(H_1H_2H_3)_{\text{cal}}|^2/|F(12,0,0)_{\text{cal}}|^2$ for the strong main reflections are plotted against $\sin \theta/\lambda$ in Fig. 9, where the observed intensity of $(12,0,0)$ reflection is normalized with the calculated value and the temperature effect is taken into account, assuming the B value in the temperature factor $\exp \{-2B(\sin \theta/\lambda)^2\}$ to be $0.5 \cdot 10^{-16} \text{ cm}^2$.^{*} The fact that the relative values observed for the lower angles considerably deviate downward from the calculated ones is most likely to be due to the primary extinction effect, since this effect is stronger for the reflections having larger structure amplitudes.

According to the theory of primary extinction,¹⁵⁾ the diffraction intensity is given by

$$I \propto f(x) \cdot |F(H_1H_2H_3)|^2. \quad (4)$$

$f(x)$ is the primary extinction coefficient for the Laue case of electron diffraction in a parallel plate crystal and is given by

$$f(x) = \sum_{n=0}^{\infty} J_{2n+1}(2x)/x, \\ x = \lambda \bar{\rho} \cdot |F|/v,$$

where J_{2n+1} is the Bessel function of the odd order, v is the unit cell volume and $\bar{\rho}$ is the effective thickness of the crystal. In order to obtain the values of $f(x)$, only the knowledge of $\bar{\rho}$ is required in the present case, since we can obtain the values of $|F|$ and v from the above mentioned structure. However, what can be obtained from the half-value breadth of intensity profile of diffraction spots is not the effective thickness of crystallites but the extension of coherent region in the film plane. Therefore, the correction of the primary extinction is performed in the following way: The values of $f(x)$ are calculated for various values of $\bar{\rho}$ and the observed intensities are corrected by these values of $f(x)$. Comparing the corrected relative intensities, $I(H_1H_2H_3)/I(12,0,0)$, with the calculated ones $|F(H_1H_2H_3)_{\text{cal}}|^2/|F(12,0,0)_{\text{cal}}|^2$,

* This value was estimated by using Debye temperature and atomic mass for the composition Au_3Mn which were calculated as arithmetic means of Debye temperature and atomic mass for component atoms. On the other hand, the B values for gold and manganese atoms were calculated to be $0.56 \cdot 10^{-16}$ and $0.52 \cdot 10^{-16} \text{ cm}^2$ respectively.

0) $_{cal}^2$, the most appropriate value of $\bar{\rho}$ was so selected that both ratios might coincide. $\bar{\rho}$ was estimated to be 80Å, and it was the same order of magnitude as the extension of coherent region in the film plane, which was measured as 100 ± 20 Å from the half-value breadth. Utilizing the former value for $\bar{\rho}$, $f(x)$ is estimated to be 0.94 for (12, 0, 0) reflection, and therefore the normalization due to this reflection is considered to be reasonable. By this procedure, the structure amplitudes $|F_{obs}|$ can be obtained from the observed intensities corrected for the primary extinction and the thermal vibration. They are tabulated in Table II. The agreement between $|F_{obs}|$ and $|F_{cal}|$ is satisfactory except the satellites flanking the main reflections. Although only the reflections with $(H_1 H_2 0)$ indices are dealt with in Table II, the circumstances are almost similar also in reflections with other indices.

§ 4. Conclusion

The present electron diffraction work has elucidated a complicated anti-phase domain structure of the ordered Au_3Mn alloy. This structure can be thought of as formed from the fundamental face-centred orthorhombic lattice ($a_1=4.08$, $a_2=4.05$, $a_3=4.03$ Å), in which the atoms arrange themselves as in the ordered structure of Cu_3Au but the two kinds of stepshift, $\pm(a_2 \pm a_3)/2$ and $\pm(a_3 \pm a_1)/2$, occur at every M_1 cells and M_2 cells along the x and y directions respectively. Thus the two-dimensional anti-phase domain structure is formed, which is considered to have a large orthorhombic unit cell belonging to the space group $Pnnm-D_{2h}^{12}$, if M_1 and M_2 are sufficiently definite throughout the lattice. This type of two-dimensional structure is different from that found in Cu_3Pd and has recently been found also in the $Cu_5Au_2Zn_3$ alloy by Wilkens and Schubert¹⁶⁾ using X-rays.* M_1 and M_2 are, however, not integers actually, even after a long period of annealing, and change from 1.0 and 2.1 to 1.3 and 2.5 respectively with the alloy composition and the heat-treatment, as described in § 3. This fractional property of domain size is common to all the

anti-phase domain structures so far examined and can be interpreted by considering a mixture of different sizes of domains, as discussed by Fujiwara, and the mode of mixture corresponding to the irregular statistical arrangement seems to occur in the present case, as described in § 3-(2). Thus, it should be noted that the model proposed in Fig. 4 and Fig. 6 corresponds to an idealized lattice of the ordered Au_3Mn , and for the actual, fractional domain size we shall not be able to define an exact unit cell.

Since the metamagnetism of the ordered alloy Au_3Mn was discovered by Meyer,⁴⁾ the alloy is being watched with great interest by many investigators of magnetism. As the magnetic property is closely connected with the crystal structure, we shall briefly consider the relation between the ordered structure of Au_3Mn obtained in the present work and the metamagnetism. From Figs. 4 and 6, it is readily known that there are two kinds of distance of manganese-manganese pairs, i.e. 2.87 and 4.05 Å. The former distance corresponds to that between manganese atoms located at an anti-phase domain boundary and seems to give rise to the antiferromagnetic interaction, while the latter is the manganese-manganese distance inside each domain and is likely to give the ferromagnetic interaction within the domain. The ferromagnetism of the disordered Au_3Mn phase is probably due to the disappearance of the regular distribution of manganese-manganese pairs with the shorter distance 2.87 Å.

The present author wishes to express his sincere thanks to Professor S. Ogawa for the kind guidance and encouragement. His thanks are due to Dr. M. Hirabayashi whose discussion was very useful, and also due to Professor A. J. P. Meyer of Université de Strasbourg who gave a valuable suggestion about the magnetic property.

The present investigation has partly been supported by the fund of the Ministry of Education in Aid of Scientific Researches.

References

- 1) E. Raub, U. Zwicker and H. Baur: *Z. Metallk.* **44** (1953) 312.
- 2) A. Kussmann and E. Raub: *Z. Metallk.* **47** (1956) 9.
- 3) A. J. P. Meyer: *Compt. rend.* **242** (1956) 2315.

* According to Wilkens and Schubert, the fundamental cell of the ordered $Cu_5Au_2Zn_3$ alloy is face-centred cubic and the domain size is $1.77a$ in either direction.

- 4) A. J. P. Meyer: *Compt. rend.* **244** (1957) 2028.
- 5) A. J. P. Meyer and P. Taglang: *J. phys. radium* **17** (1956) 457.
- 6) S. Ogawa and D. Watanabe: *J. Phys. Soc. Japan* **9** (1954) 475.
- 7) D. Watanabe and S. Ogawa: *J. Phys. Soc. Japan* **11** (1956) 226.
- 8) D. Watanabe: to be published.
- 9) D. Watanabe: to be published.
- 10) H. Bumm and U. Dehlinger: *Metallwirtsch.* **13** (1934) 23.
- 11) J. M. Cowley: *Acta Cryst.* **6** (1953) 516.
- 12) J. Karle and I. L. Karle: *J. Chem. Phys.* **18** (1950) 957.
- 13) K. Fujiwara: *J. Phys. Soc. Japan* **12** (1957) 7.
- 14) P. Perio and M. Tournarie: *Acta Cryst.* **12** (1959) 1032.
- 15) M. Blackman: *Proc. Roy. Soc. A*, **173** (1939) 68.
- 16) I. Waller: *Ann. Physik* **79** (1926) 261.
- 17) M. Wilkens and K. Schubert: *Z. Metallkde.*, **48** (1957) 550.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Re-appreciation of the Second Order Transition Phenomena in Polyethylene

By Ryuichi NAKANE

Electrical Communication Laboratory, Musashino-shi, Tokyo

(Received November 12, 1950)

The second order transition phenomena in polyethylene are discussed based on our dilatometric measurement. Calculating the value $(V_1 - V_0) / (V_2 - V_0)$ from the result of measurement on three samples, each having different crystallinity, it is found that the crystallinity of polyethylene changes with temperature above -30°C . Also the transition at -55°C is found, below which the expansion coefficient of crystalline phase becomes equal to that of amorphous phase, and this phenomenon is thought to be the true second order transition. The crystallinity of each sample is calculated by using the method of Hoffmann and Weeks as the first approximation and applying some further calculation. The application of the least-mean-square method to the decision of transition by means of the electronic computer is attempted.

§1. Introduction

So many values were hitherto suggested as the second order transition temperature of polyethylene, each by different author,^{3), 5) - 7)} and none has ever discussed which of them is the true second order transition point. And the nature of this transition was nearly unknown, though several hypothetical considerations should have been made.

We have previously carried out some dilatometric measurements on polyethylene in the range higher than the room temperature, and recently in the low temperature range. From these experimental results we tried to get some knowledge on the second order transition phenomena and on the crystalliza-

tion of this polymer as far as possible.

§2. Method of Experiment and Sample

The usual Bekkedahl type glass dilatometer¹²⁾ was used throughout our experiment. As the filling liquid we adopted *n*-propyl alcohol faintly coloured with a trace of Sudan Black, but special cautions were needed for the use of the liquids like this. Such organic liquid had about three times higher expansion coefficient than polyethylene itself, and the equilibrium of temperature between the filling liquid and the bath was rather doubtful, especially in the low temperature range. So if the measurement of temperature was carried out with some error, it would result

the three times larger error in the specific volume of sample, and the following technique was necessary for the precision of measurement.

In our experimental equipment, in addition to the dilatometer tube a short tube was set which was also filled with *n*-propyl alcohol and a copper-constantan thermocouple was inserted into it. The equilibrium of temperature between the filling liquid of dilatometer and of this tube was thought to be sure, and in the blank test the relation between the thermoelectric force of the couple and the specific volume of *n*-propyl alcohol was calibrated and after the main experiment this relation was used to calculate the specific volume of sample.

The low temperature bath was a domestic thermos jar filled with denatured alcohol. Crushed dry ice was added into it and low temperature of -76°C was performed. (Of course performance of -78°C was possible, but it required an excess amount of dry ice and the elevation of temperature was hereafter too slow till the excess dry ice evaporated away, only meant loss of experimental time.) The elevation of temperature was proceeded with a speed of about 0.1°C per minute by means of a hand-made electric heater. Measurements were done at every ten minutes.

Seven samples were prepared for our experiment. Marlex 50/15, usually thought to have the same nature as the low pressure polyethylene, and Alathon 10, a typical high pressure polyethylene, were each measured in the state of original pellet, in the state melted and quenched to the dry ice temperature, and in the state melted and annealed gradually. And as the abnormally low molecular weight sample, DYGT, molecular weight of about 7000 and thought to have much molecular chain branching, was adopted. This sample was vacuum-melted to remove the gas foam occluded in the original pellet and cooled simply, as it had too high fluidity in the melted state and delicate heat-treatment was difficult. In the succeeding description these samples will be written abbreviatedly as M_n , M_q , M_a , A_n , A_q , A_a , and G .

§ 3. Decision of Transition Point

Some of our experimental results are shown

in Figs. 1, 2, 3. The direct decision of transition point from these curves is rather difficult and subjective, though many authors have adopted this direct method.^{3), 4)} If such

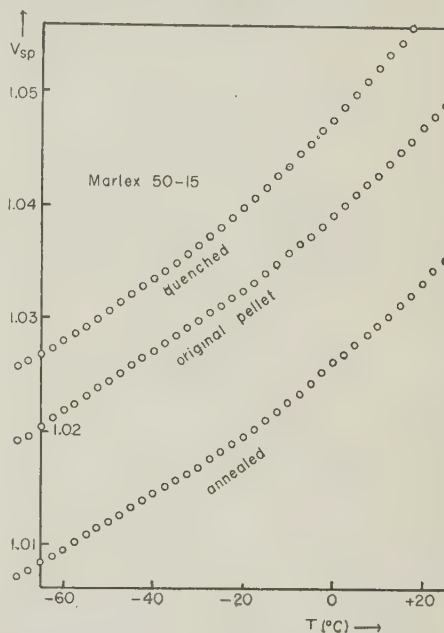


Fig. 1. The experimental relations between the temperature and the specific volume in Marlex 50/15.

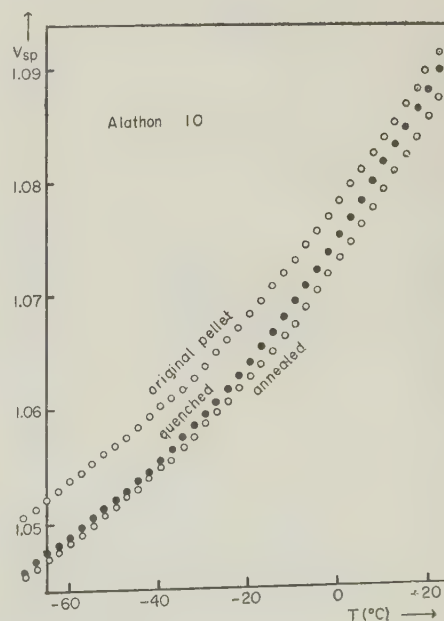


Fig. 2. The experimental relations between the temperature and the specific volume in Alathon 10.

a curve is perfectly a crossing of two lines, the decision of the crossing point is possible by means of a least-mean-square method as will be described in the Appendix of this article, but these temperature vs. specific volume curves essentially have nature of

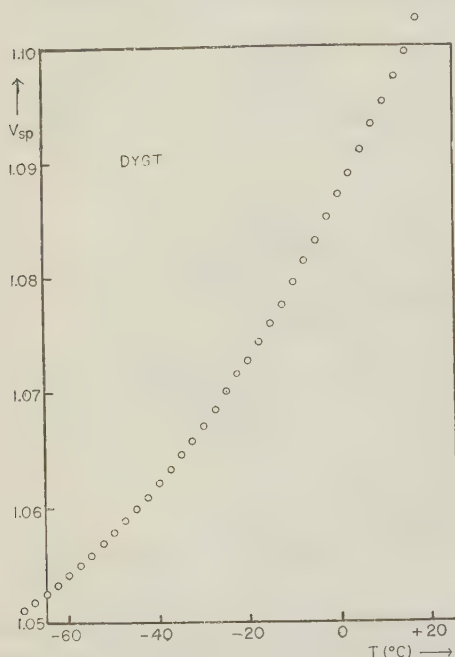


Fig. 3. The experimental relations between the temperature and the specific volume in DYGT.

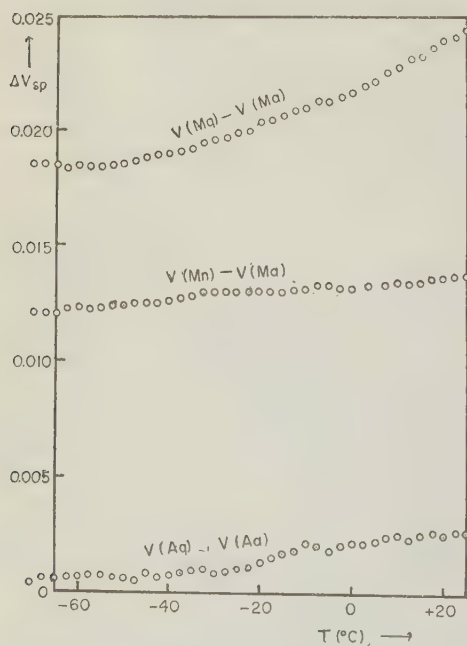


Fig. 4. Difference between the specific volume of various polyethylene samples.

higher order, and the approximation of it by a crossing of two lines is actually unreasonable. So some discussion is necessary before the decision of the transition point from our experimental result.

By plotting the difference between the specific volume of quenched Marlex and annealed Marlex against the temperature, we got the plot shown in Fig. 4. In this figure it is clearly seen that this value becomes constant below -55°C . This means that below this temperature the relation

$$\frac{dV_o}{dT} = \frac{dV_a}{dT} \quad (1)$$

stands. It suggests the presence of the second order transition at this point as Kovacs⁴) referred to it. Here V_o is the specific volume of pure crystalline phase and V_a is that of pure amorphous phase.

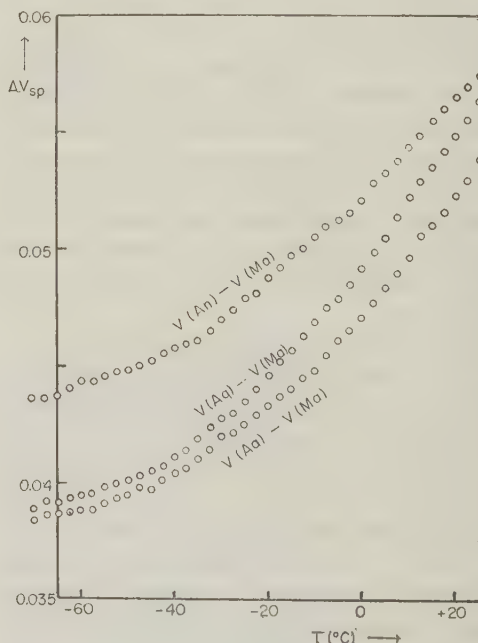


Fig. 5. The same as Fig. 4, showing the other part.

The crystallinity of polymer is usually defined as

$$\theta = \frac{V_a - V}{V_a - V_c}$$

if based on dilatometric data. If the measurements are done on three samples, each having the different crystallinity, the equation

$$\frac{\theta_1 - \theta_0}{\theta_2 - \theta_0} = \frac{V_1 - V_0}{V_2 - V_0}$$

stands at any temperature, even if V_a or V_o has some discontinuous points. If the crystallinity does not change with temperature, the right hand side of this equation should be a constant independent of temperature. On the contrary, if the right hand side of this equation varies with temperature, this is the sufficient condition for the crystallinity change. The word 'sufficient' is needed, because if the crystallinity changes in linear form as

$$\theta(T) = \theta(T_0) + a(T)\theta(T_0) + b(T) \quad (3)$$

this value also remains constant.

Calculating the value

$$K(T) = \frac{V(M_n) - V(M_a)}{V(M_o) - V(M_a)} \quad (4)$$

from our experimental data we get the result shown in Fig. 6. From this we find that the crystallinity of this polyethylene has changed at least above -30°C . The value -21°C ,

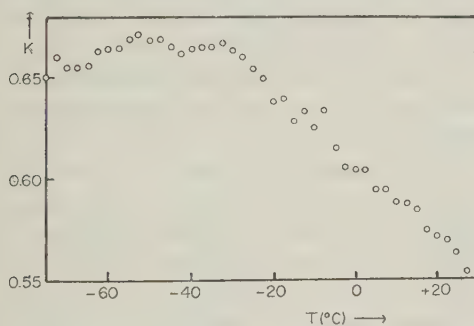


Fig. 6. K -value test. The change of this value is the sufficient condition for the change of crystallinity.

reported by Danusso and others³⁾ as the second order transition point of polyethylene, should correspond to this value, shifted in the process of defining transition, because they defined the transition as the break point of line, and we defined it as the beginning of change in our K -value test.

§ 4. Calculation of Crystallinity

Hoffman and Weeks⁹⁾ calculated the crystallinity of polychlorotrifluoroethylene from its specific volume and second order transition point. Their method can be applied to polyethylene if its second order transition point is clearly known, and an introductory descrip-

tion about their method is here necessary.

In the temperature range where the crystallinity of polymer substance does not change with temperature,

$$\theta_1 = \frac{V_l - V_1}{V_l - V_o} = \left(\frac{dV_l}{dT} - \frac{dV_1}{dT} \right) / \left(\frac{dV_l}{dT} - \frac{dV_o}{dT} \right) = \frac{V_l' - V_1'}{V_l' - V_o'} \quad (5)$$

$$\theta_2 = \frac{V_l - V_2}{V_l - V_o} = \frac{V_l' - V_2'}{V_l' - V_o'} \quad (6)$$

where V_l is the specific volume of the liquid phase. From these equations we have

$$V_l(V_1' - V_2') + V_l'(V_2 - V_1) = V_2V_1' - V_1V_2' \quad (7)$$

If V_1 can be represented as

$$V_l = A + BT + CT^2, \quad (8)$$

substituting it into (7) we get

$$\begin{aligned} A(V_1' - V_2') + B\{(V_2 - V_1) + T(V_1' - V_2')\} \\ + C\{(V_1' - V_2')T^2 + 2T(V_2 - V_1)\} \\ = V_2V_1' - V_1V_2' \end{aligned} \quad (9)$$

On the other hand if the specific volume of the sample is measured at two points in the temperature range higher than the melting point, we have

$$V_l(T_1) = A + BT_1 + CT_1^2 \quad (10)$$

and

$$V_l(T_2) = A + BT_2 + CT_2^2 \quad (11)$$

A , B , and C can be calculated from (9), (10) and (11), and in this way we get the complete representation of V_l . For the calculation of V_o , the change of slope at the second order transition point, $\Delta\alpha$, is used. This angle should be proportional to $(1 - \theta)$, or the content of the amorphous part, so long as the second order transition is thought to appear only in the amorphous part. On the other hand, the crystallinity should be proportional to $V_l - V$, and so for two samples of different crystallinity

$$1 = \theta_1 + (1 - \theta_1) = a\Delta V_1 + b\Delta\alpha_1 \quad (12)$$

$$1 = \theta_2 + (1 - \theta_2) = a\Delta V_2 + b\Delta\alpha_2 \quad (13)$$

stand, and from these two equations we can get a and b , and the crystallinity of these two samples can be calculated.

Hoffman and Weeks' method has its unreliability in using the first order derivatives of the experimental curves, which are thought to be of less accuracy, but this method can be used as the first order approximation in

our calculation.

Following to our experimental data we find that

$$V=1.0306 \quad V'=0.00029 \quad \text{for } M_q$$

$$V=1.0200 \quad V'=0.00025 \quad \text{for } M_a$$

at -50°C , and from our previous measurement²⁾

$$V_i(+120^\circ\text{C})=1.2600$$

$$V_i(+150^\circ\text{C})=1.2885.$$

From these we get

$$\left. \begin{aligned} A &= 1.1641 \\ B &= 0.000666 \\ C &= 0.0000011 \end{aligned} \right\} \quad (14)$$

by solving the equations (9), (10) and (11).

As described above, we have seen that below -55°C

$$V_b' = V_a' = 0.000234.$$

Equation (14) gives $V_i' = 0.000654$, and so for a pure amorphous sample the change of slope at this point should be 0.000420.

With our experimental data for M_a the change of slope in the T vs. specific volume curve at -55°C was evaluated as 0.000020 or 0.000015. From the ratio of this value to the value 0.000420 the crystallinity of M_i can be calculated as 95 or 97%. This value cannot be expected of much high accuracy, so we assume it as 95%. From this evaluation the crystallinity of M_q is calculated by using

$$\left. \begin{aligned} V_i(-55^\circ\text{C}) &= 1.1308 \\ V_q(-55^\circ\text{C}) &= 1.0292 \end{aligned} \right\} \quad (15)$$

and we get the value of 80.4%. The difference between the crystallinity of M_a and M_q is 14.6% in this approximation, and the change of slope in the experimental curve at -55°C is 0.000044, so it should be 0.000301 for pure amorphous sample, not consistent with the above calculated value 0.000420.

Here our calculation proceeds to the second approximation. Leaving from the method of Hoffman and Weeks and assuming the change of slope at -55°C is

$$0.000301 + 0.000234 = 0.000535$$

for pure amorphous sample and again using the value of V_i at 120°C and 150°C , the coefficients A , B , C are again calculated. In this way we get

$$\left. \begin{aligned} A &= 1.1657 \\ B &= 0.000655 \\ C &= 0.00000109 \end{aligned} \right\} \quad (16)$$

and

$$\left. \begin{aligned} V_i &= 1.1330 \\ V_e &= 1.0050 \\ (V_i - V_b) &= 0.1280 \\ \theta(M_i) &= 95.4\% \\ \theta(M_q) &= 81.0\% \\ \Delta\alpha(0\%) &= 0.000306 \end{aligned} \right\} \quad (\text{at } -55^\circ\text{C})$$

Calculation of V_e in the temperature range where it changes is a little conventional. Assuming $\theta(M_a)$ does not vary with temperature we get the first approximation curve of T vs. $\theta(M_q)$. But $\theta(M_i)$ itself should change with temperature also, so we assume that this change is proportional to $(1-\theta)$ though it is a little inconsistent with the principle of the above described K -value test, and get the curve shown in Fig. 7. This calculation is done without using the principle of K -value test, and so we again prove the change of crystallinity above -30°C .

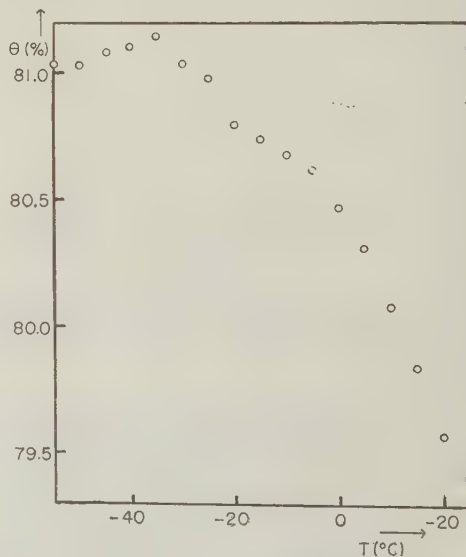


Fig. 7. Change of crystallinity with temperature in quenched Marlex.

Our now described calculation contains the evaluation of V_e , and making it continuous with the slope below -55°C , we get

$$\begin{aligned} A' &= 1.0203 \\ B' &= 0.000337 \\ C' &= 0.00000103 \end{aligned}$$

for the coefficients of

$$V_o = A' + B'T + C'T^2.$$

Below -55°C , obviously

$$V_o = 1.0019 + 0.000234(T + 55)$$

$$V_g = 1.1300 + 0.000234(T + 55).$$

Where V_o means the specific volume of the non-crystalline phase under the second order transition point.

§ 5. Result on High Pressure Polyethylene

The same process of analysis as above might be applied to our experimental data on high pressure polyethylene, but in doing so we met some difficulties. One of these was that the specific volume of this polyethylene did change only a few amount by heat treatment such as quenching or annealing. In addition to this, the specific volume of original pellet of Alathon was sometimes higher than that of quenched one, and its T vs. V_{sp} curve was a little anomalous as shown in Fig. 2, namely it showed the specific volume quite near to that of A_q at room temperature and considerably higher value compared with that of A_q at dry ice temperature.

These phenomena should have originated from some residual stress left in this sample. The presence of this stress was made visible by heating a piece of Alathon 10 at 150°C for several minutes. The pellet which at first cubelike shaped turned into a narrow ribbon, about 2 times elongation in two directions and nearly $1/2$ times contraction in one direction. The pellet of Alathon should have been made by cutting into pieces a hot-rolled plate, so having some residual shear stress frozen in it. So when we are going to measure some quantities on such pellet, care must be taken on this point. (the pellet of Marlex was short-cut cylinder shaped and our above discussion should have been quite safe on this point.)

In spite of these difficulties, we tried to apply the same method to our experimental data on high pressure polyethylene. The value $V(A_q) - V(A_a)$ is shown in the lowest place in Fig. 4. In this curve, we can see that about below -47°C this value becomes constant, and this point should be thought as the second order transition point of high pressure polyethylene.⁵⁾ It is rather probable that low pressure polyethylene and high

pressure polyethylene have each different second order transition point, but the value $V(A_q) - V(A_a)$ is smaller than the value $V(M_q) - V(M_a)$, so of less accuracy, and this difference of the transition points may contain some experimental error.

As shown in Fig. 5, the value $V(A_q) - V(M_a)$ or $V(A_a) - V(M_a)$ did not become constant even below -55°C , only became linear about below -47°C . If our above considerations are right, this means that either V_l or V_o or both of them are not of the same value for M and A . In the temperature range higher than the melting point, the specific volume of every polyethylene was nearly on a same line, so in the first sight V_l seems to do not change with sample kind. But in a half crystallized sample, the amorphous part may have higher concentration of methyl groups than the melted one, so it is probable that V_l of different polyethylenes are each different at a temperature far below the melting point. And saying about V_o , the X-ray diffraction pattern gives larger lattice constant for high pressure polyethylene than for low pressure polyethylene. Thus both V_l and V_o may possess different values for dif-

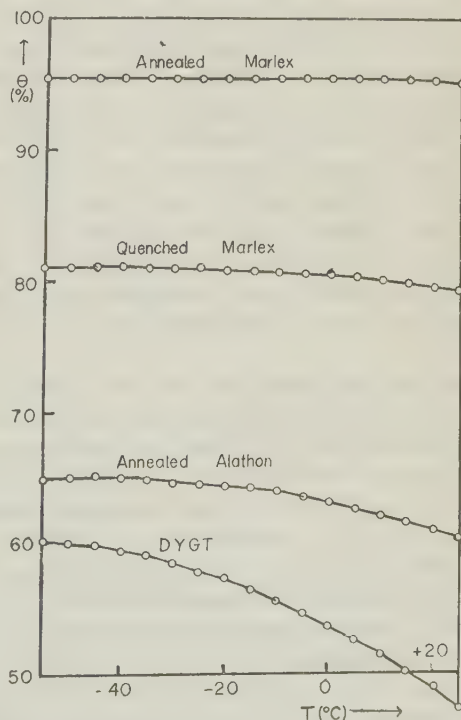


Fig. 8. Change of crystallinity with temperature in various samples.

ferent polyethylenes. But to take into account these variation of V_i and V_o makes the definition of crystallinity too tedious, as in doing so we must decide V_i and V_o at least of the function of molecular chain branching.

Considering these situations, we calculated the crystallinity of Alathon and DYG as the function of temperature simply using our above described relations, and showed it in Fig. 8. From this we can see that the crystallinity of Alathon changes above -35°C . And saying about DYG, this polyethylene has about the same crystallinity as Alathon at low temperature, and its melting range spreads deeply into the low temperature region and so shows the larger volume than Alathon at room temperature. Its crystallinity change transition may lie at -50°C or lower, and almost covered by the transition at -55°C or -47°C .

§ 6. Mechanism of Transitions

The mechanism of the second order transition cannot be said to have been clearly known at present stage even for non-crystalline polymer. The existing theories of this phenomena are the one based on the intramolecular rotation of chain element and its frozen-in at low temperature,¹⁰⁾ and the one chiefly based on rheological consideration.¹⁾ The second order transition in crystalline polymer is usually thought to happen only in its non-crystalline part, a quite natural presumption, but as we discussed above the interaction between the crystalline part and the amorphous part is not negligible and this should be taken into consideration in some case.

Our previous experiment on the increase of crystallinity in the melting range and its memory phenomena²⁾ was well interpretable as the growth of crystallite size; and the shape of T vs. V_{sp} curve was also interpreted with the concept of crystallite size distribution. The smaller sized crystallite suffers more effect from surface energy, so shows the lower melting point. If this concept is right, at some low temperature the crystallinity should cease to change with temperature. Previously we described this means the second order transition, but our new experiment showed that this phenomena, if exist, may correspond

to the crystallinity change transition at -30°C . Our previous calculation²⁾ gave the value for this transition in polyethylene as -35°C or -40°C , a quite good agreement with the experimental result comparing with the roughness of our assumption.

The theory of Kovacs⁴⁾ which treats polyethylene as the mixture of low molecular normal paraffins considering the fact that the main chain of this polymer molecule is effectively cut into shorter sub-chains at the points where the side chains exist so long as the crystallization phenomena concern, is also able to interpret these experimental results. In the melting range the sample having unsaturated crystallinity increases its crystallinity as the consequence of sub-chain aggregation having the melting point higher than the temperature at which it kept, and the shape of T vs. V_{sp} curve itself tells the distribution of sub-chain length, and the crystallinity change transition corresponds to the shortest sub-chain length.

However, our experiment showed that even Marlex which was thought to have few chain branchings changed its crystallinity in enough low temperature range, a phenomenon not interpretable directly with his concept. On the other hand, the fact that the more branched polyethylene shows the wider melting range is quite naturally understood with his concept, which is also able to be elucidated with our concept of crystallite size distribution as its size is restricted by the presence of side chain. Kovacs' concept and ours may be of the same nature ultimately if the calculations are carried out completely, but at present stage the concept of crystallite size distribution is thought to be more natural, because the presence of surface energy may part some role in the crystallization phenomena¹³⁾

For the transition at -55°C , which have been supposed to be the true second order transition, only a rough description can be given hypothetically. The fact that the crystallinity does not change below -30°C means that there remains no amorphous part which is able to crystallize, as it suffers considerable traction from neighbouring crystalline part. The crystallite is supposed to have strong anisotropic expansion coefficient,¹¹⁾ and as the temperature lowered this traction may

become stronger, at last at one temperature, probably -55°C , the volume of amorphous part becomes to change only in the same ratio as the crystalline part, and the change of temperature only causes change of traction in the amorphous part. Speaking more schematically, the amorphous part becomes to be completely besieged by the crystalline part and cannot expand or contract freely.

However, there exist some other ways of interpretation. One of them is that even below -30°C the crystallinity still continues to change, for our K -value test tells only the sufficient condition of crystallinity change, and moreover, because of the amorphous part suffers considerable tension as the result of volume constriction in crystallization, the amorphous part may have lower density than the liquid phase, so the increase of density by crystallization is almost compensated by this effect, and at -55°C the crystallinity ceases to change and here the transition appears. But the test of such possibility cannot be judged by the dilatometric experiment only.

The author wishes to express his sincere thanks to Dr. K. Nagamatsu for his suggestion on the necessity of the absolute decision of the transition point, and to Dr. A. Nishio for his kind discussions and advices.

Appendix. Determination of the Transition Point by Electronic Computer

When some experimentally measured points are thought to have enough reasons being distributed on two lines as shown in Fig. 9, its breaking point can be decided by least-

mean-square method.

Firstly we place the imaginary breaking point between 2 and 3 and decide two lines separately with least-mean-square method by using the points from 1 to 2 and from 3 to 11, and calculate the deviation $\sum \delta_i^2$ of these points from these lines.

Then shifting the breaking point to the position between 3 and 4, the deviation is again calculated in the same way. By repeating this process, the deviation should show its minimum value when the breaking point is placed at its appropriate position according to the principle of least-mean-square method.

As the number of points increases, this calculation turns to be so enormous one that the computation by usual method becomes practically impossible.

The electronic computer $M-1$ in our Laboratory can be used for this problem. As the testing data we adopted the result of our experiment on original pellet of Marlex in the temperature range from -35°C to $+25^{\circ}\text{C}$, using mercury as the filling for the sake of precision. 41 points were measured, and these

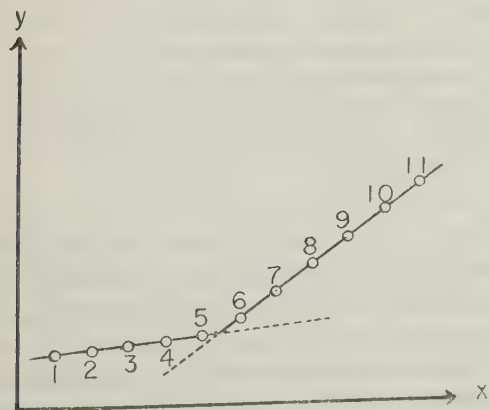


Fig. 9. Schematic diagram interpreting the principle for the decision of transition.

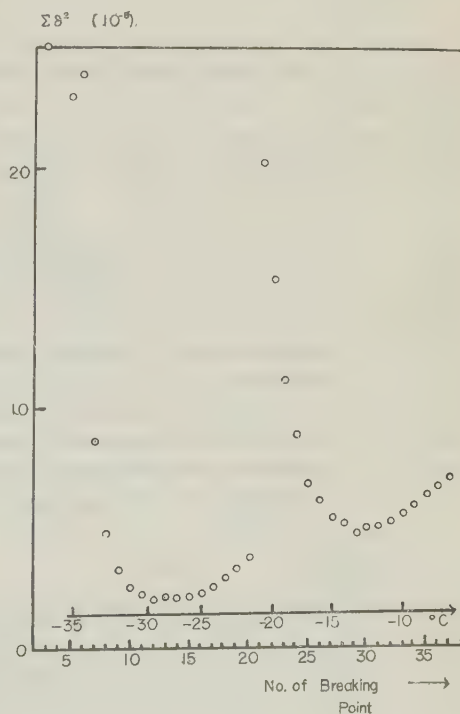


Fig. 10. Decision of the transition by least-mean-square method. The deviation should show its minimum at the transition point.

values were converted to a form adapting to the technical requirements of this computer.

The result of our calculation is shown in Fig. 10. The deviation showed its minimum at -28°C , a reasonable result, but the abrupt change at -20°C is quite uninterpretable.

As described above, this T vs. V_{sp} curve could not be said of a linear form, and if a point near the real breaking point was a little shifted downward by some experimental error, this point has much possibility to be judged apparently as the breaking point. In addition to this, our measured points were distributed unbalancingly below and above the crystallinity transition point, and this might have also caused some error.

After all, as this point at -30°C or -28°C should not be the true second order transition point as described above, our present method rather should be applied to the true second order transition at -55°C , by converting the experimental data as possible as linear form in reasonable way. There may exist many other phenomena in various fields of science

on which our calculating method is applicable.

References

- 1) R. F. Spencer and R. F. Boyer: *J. Appl. Phys.* **17** (1946) 398.
- 2) R. Nakane: *J. Polymer Sci.* **31** (1958) 244 and the full manuscript referred in it.
- 3) F. Danusso et al.: *ibid.* **21** (1956) 139.
- 4) A. J. Kovacs: *ibid.* **34** (1959) 551.
- 5) P. W. Jensen: *ibid.* **28** (1958) 635.
- 6) M. L. Dannis: *J. Appl. Polymer Sci.* **1** (1959) 121.
- 7) S. M. Ohlberg and S. S. Festermarker: *J. Polymer Sci.* **32** (1958) 514.
- 8) H. Mark and G. S. Whitby: *Advances in Colloid Sci.* **2** (1946).
- 9) J. D. Hoffman and J. J. Weeks: *J. Polymer Sci.* **28** (1958) 472; *J. Research N. B. S.* **60** (1958) 465.
- 10) For example, J. H. Gibbs and E. A. DiMartio: *J. Chem. Phys.* **28** (1958) 373.
- 11) C. W. Bunn and T. C. Alcock: *Trans. Soc.* **41** (1945) 317.
- 12) N. Bekkedahl: *J. Research N.B.S.* **43** (1949) 145.
- 13) C. W. Smith and M. Dole: *J. Polymer Sci.* **20** (1956) 37.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

The Binding Energy of the σ Bond, I. General Theory

Kiyosi O-OHATA

*Physics Department, Tokyo Institute of Technology,
Oh-okayama, Meguro-ku, Tokyo*

(Received November 17, 1959)

In the calculation of the binding energies of σ bonds, it is necessary to take full account of the overlap integrals between bonded orbitals, but it is sufficient to take up to the second order terms for the overlap integrals between non-bonded orbital into account, because the magnitude of the latter overlap integrals is much smaller than that of the former integrals. The binding energy of a σ bond in the above approximation is discussed.

§ 1. Introduction

It is hardly necessary to mention here how fruitful the concept of the bond proved to be, particularly in organic chemistry where the additive rules of the bond energies and the bond moments have served so well. Since, however, there are many objections against the additive character of the bond properties,

it may be desirable to study the molecule consisting of only σ bonds (We shall call it the saturated molecule.) by the use of quantum mechanics. The attempt for doing this has hitherto been undertaken by using the approximate method of electron pair bonds, which assumes the following simplifications.⁽¹⁾

- (1) Each atom is promoted to an appropriate

valence state.

(2) Valence orbitals are linked together in pairs to form chemical bonds, so that only one pairing scheme needs to be considered.

(3) The non-orthogonality between the valence orbitals is neglected.

(4) In spite of the above assumption, the overlaps between the valence orbitals in the exchange terms in the energy expression are taken into account.

(5) All ionic terms are neglected.

The first assumption was investigated for methane by several authors,⁽²⁾ and they obtained the result that the effect due to including all the valence states in the s^2p^2 and sp^3 electron configurations of the carbon atom may not give rise any appreciable contribution to the value of the binding energy of methane evaluated under the assumption of the tetravalent carbon atom. Thus, we shall not discuss further this problem. The second assumption is kept in our discussion and this may be plausible at least for the ground states of the saturated molecules. The third and fourth assumptions are very serious because of the two reasons the one that the assumptions themselves are not consistent and the other that the overlap integrals between paired orbitals are not generally so small to be neglected. The main object of this article is to discuss the problem due to the non-orthogonality of the orbitals. The last assumption is not valid in the discussion of the bond moment and appropriate ionic terms should be included, but will not be discussed in the present article.

§2. Wave Functions

Usually, a description of a bond is given in terms of both of the directional valence orbitals, wherein valence orbitals project out along the directions from the individual atoms to the attached atoms, and of electron pairing, wherein the spins of two electrons in paired orbitals should be anti-parallel. Thus the wave function of a bond $A-B$ connecting two atoms A and B is expressed as

$$\phi_{ij}(1, 2) = \phi_i(1)\phi_j(2)\frac{1}{2}(\alpha(1)\beta(2) - \beta(1)\alpha(2)), \quad (2.1)$$

where ϕ_i and ϕ_j are the atomic valence orbitals of the atoms A and B , respectively, and they are given by promoting each atom to an appropriate valence state to describe the directional character above mentioned. In Eq.

(2.1), $\frac{1}{2}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ is the spin part of the wave function, and 1 and 2 denote the coordinates of the 1st and 2nd electrons, respectively. This approximate description corresponds to the so-called Heitler-London method, but there is another extreme method to describe the chemical bond, namely the molecular orbital method.⁽³⁾ In the molecular orbital method we use a molecular orbital τ , which is localized in the region of the bond $A-B$, as the directional orbital instead of the atomic orbitals ϕ_i and ϕ_j in Eq. (2.1).^{*} The molecular orbital τ is usually expressed as a linear combination of the atomic orbitals ϕ_i and ϕ_j . There is, of course, another point of view intermediate between the above two methods, in which we define a pair of semi-localized bond orbitals χ_i and χ_j by

$$\begin{aligned} \chi_i &= \frac{1}{\sqrt{1+2\lambda S_{ij}+\lambda^2}}(\phi_i + \lambda\phi_j), \\ \chi_j &= \frac{1}{\sqrt{1+2\mu S_{ij}+\mu^2}}(\phi_j + \mu\phi_i), \end{aligned} \quad (2.2)$$

where S_{ij} is the overlap integral between ϕ_i and ϕ_j , and λ and μ are parameters to be determined by the condition of minimizing the total energy of the molecule. χ_i and χ_j are used as the directional valence orbitals. This method includes both of the previous two methods as the extreme cases, and may be more preferable because of its adequate cognizance of the correlational repulsion between pairing electrons and its inclusion of ionic terms in the individual chemical bonds. Then, we use an orbital pair to describe a chemical bond and a set of orbitals pairs to represent the constituent chemical bonds of a saturated molecule, whichever we choose in the previous three methods. In addition, each atom in the molecule generally has several orbitals which are filled up by two electrons with opposite spins. Hereafter we shall call these simply core orbitals. It is, however, not necessary to distinguish the difference between the valence and core orbitals in general formulae, because of the same spin dependence in both cases. Thus, the wave function of the total system can be obtained by the assumption that each of the orbital pairs, $(\phi_i, \phi_j)(\phi_k, \phi_l), (\phi_p, \phi_q), \dots$, is occupied by the two electrons

* The relation between the methods of localized and non-localized molecular orbitals was discussed by Coulson.⁽¹⁾

which are coupled to form a singlet. These paired orbitals are either the appropriate valence orbitals being in charge of a chemical bond or the same orbitals representing an atomic core. Although we shall adopt the description of a bond in the Heitler-London method, the expression for the total energy is applicable in the other two methods, *mutatis mutandis*.

By the above consideration, the primitive wave function Ψ^0 of the molecule composed of r orbital pairs is expressible as a product of wave functions for the orbital pairs:

$$\Psi^0 = \Theta^0 \Theta = \phi_{ij}(1, 2) \phi_{kl}(3, 4) \cdots \phi_{pq}(2r-1, 2r), \quad (2.3)$$

where Θ^0 and Θ are the orbital and spin parts of the wave function, respectively, and ϕ_{ij} is the wave function (2.1) and so on. From the primitive function Ψ^0 , we can construct the total wave function of the molecule Ψ :

$$\Psi = \sum_P \epsilon^P P \Psi^0, \quad (2.4)$$

where P denotes a permutation of the whole electrons, ϵ^P is +1 or -1 according as P is even or odd, and the summation is taken over all permutations.

§ 3. Discussion on Non-orthogonality

If $\mathcal{H}$ is the Hamiltonian of the entire system, the total energy of the molecule is calculated by the equation

$$E = \frac{\sum_P U(P) H(P)}{\sum_P U(P) A(P)}, \quad (3.1)$$

where $U(P) = \int \Theta P \Theta d\sigma$ and this integration is taken over the spin coordinates of all the electrons. Throughout the article, we assume the wave functions to be real, and then we have

$$\left. \begin{aligned} H(P) &= \int P \Theta^0 \mathcal{H} \Theta^0 dV, \\ A(P) &= \int P \Theta^0 \Theta^0 dV, \end{aligned} \right\} \quad (3.2)$$

where the integrations are taken over the coordinates of all electrons.

Before the detailed discussion of Eq. (3.1), we shall consider the problem of the non-orthogonality. In any of the three methods in the preceding section, overlap integrals may be classified into two classes with respect to their magnitude, namely the overlap between

paired orbitals and the one between unpaired orbitals. Usually, the magnitude of overlap integrals between paired orbitals is so large that they should be thoroughly taken into account in the calculation of any physical quantity of the molecule. On the other hand, the magnitude of overlap integrals between unpaired orbitals is very smaller than unity, and it may be plausible to neglect the quantities of the order of higher than third power of the overlap integrals between unpaired orbitals.

The state of affairs corresponds to take only the following two types of permutations in Eq. (3.2) into consideration. The first consists of the permutations which are written in the form of products of interchanges between electrons in paired orbitals (P_0 will be used to designate a permutation of this type.) and the second consists of the permutations which can be written in the form of products of an interchange between electrons in unpaired orbitals and P_0 's (A permutation of the second type will be denoted by P_1). According to the assignment of the numbers to the electrons in Eq. (2.3), they can be expressed as

$$\left. \begin{aligned} P_0 &= (1, 2)^{\lambda_1} (3, 4)^{\lambda_2} (5, 6)^{\lambda_3} \cdots (2r-1, 2r)^{\lambda_r}, \\ P_1 &= (2m-1, 2n) P_0, \quad m \neq n, \end{aligned} \right\} \quad (3.3)$$

where any of $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_r$ takes the values of either 0 or 1 independently each other, and m and n are positive integers.

Under the approximation above mentioned, the value of the total energy of the molecule (3.1) becomes

$$E \cong \frac{H_0 + H_2}{A_0 + A_2}, \quad (3.4)$$

where

$$\left. \begin{aligned} H_0 &= \sum_{P_0} U(P_0) H(P_0), \quad A_0 = \sum_{P_0} U(P_0) A(P_0), \\ \text{and} \\ H_2 &= \sum_{P_1} U(P_1) H(P_1), \quad A_2 = \sum_{P_1} U(P_1) A(P_1). \end{aligned} \right\}$$

H_2 and A_2 are the quantities of the second order in the overlap between unpaired orbitals. We will use different notations for the above two kinds of overlap integrals, namely S_{ij} for the overlap integral between paired orbitals ϕ_i and ϕ_j , and T_{ik} for the one between unpaired orbitals ϕ_i and ϕ_k . Then we have

$$A_0 = \prod_{(i,j)} (1 + S_{ij}^2), \quad (3.6)$$

and

$$A_2/A_0 = -\frac{1}{2} \sum_{\{(ij)(kl)\}} A(ij, kl), \quad (3.7)$$

where

$$A(ij, kl) = \frac{1}{(1+S_{ij}^2)(1+S_{kl}^2)} \{ T_{ik}^2 + T_{il}^2 + T_{jk}^2 + T_{jl}^2 + 2S_{ij}(T_{ik}T_{jk} + T_{il}T_{jl}) + 2S_{kl}(T_{ik}T_{il} + T_{jk}T_{jl}) + 2S_{ij}S_{kl}(T_{ik}T_{jl} + T_{il}T_{jk}) \}. \quad (3.8)$$

$A(ij, kl)$ comes from the non-orthogonality between two orbital pairs (ϕ_i, ϕ_j) and (ϕ_k, ϕ_l) . The product in Eq. (3.6) extends over all orbital pairs, and the summation in Eq. (3.7) over all pairs of orbital pairs. It should be here noted that so far as the non-orthogonality resulting from the overlaps between valence and core orbitals is concerned, the difficulty can be overcome in the following way. We can take a new atomic valence orbitals $\tilde{\phi}_i^A$ in place of the atomic valence orbital ϕ_i^A of an atom A:

$$\tilde{\phi}_i^A = \frac{1}{\sqrt{1 - \sum_{\nu} T_{i\nu}^2}} (\phi_i^A - \sum_{\nu} T_{i\nu} \phi_{\nu}^B), \quad (3.9)$$

where ϕ_{ν}^B is a core orbital of the atom B which is bonded to the atom A by ϕ_i^A and $T_{i\nu}$ is the overlap integral between ϕ_i^A and ϕ_{ν}^B . $\tilde{\phi}_i^A$ may be assumed to be orthogonal to core orbitals of other atoms, since it may be plausible to neglect overlap integrals between ϕ_i^A and core orbitals of other atoms than the atom B and those between core orbitals in different atoms. Though we shall not use $\tilde{\phi}_i$ but use ϕ_i for the valence orbital, but we will assume all the valence orbitals to be orthogonal to all the core orbitals. This defect can be easily removed by using $\tilde{\phi}_i$ in place of ϕ_i . In Eq. (3.6) it is, therefore, sufficient to consider overlaps between unpaired valence orbitals. Let us here assume that the saturated molecule under consideration is composed of N equivalent atoms, individual atoms have n neighbours linked by n chemical bonds, the pairs of orbitals pairs (ϕ_i, ϕ_j) and (ϕ_k, ϕ_l) with non-vanishing $A(ij, kl)$ corresponds to the

neighbouring chemical bonds, and $A(ij, kl)$'s have a common value δ . From Eq. (3.7) it follows that $A_2/A_0 = -\frac{1}{4}n(n-1)N\delta$, if we neglect the edge effect. Usually, δ can be assumed to be very smaller than unity, but A_2/A_0 is not small. Thus, we cannot generally expand $(1+A_2/A_0)^{-1}$ as a power series of A_2/A_0 except for small molecule in which N is small. We assume, however, the cancellation of the terms resulting from higher order permutations and postulate the possibility of the above expansion. Thus, the approximate value of the total energy of the molecule is calculated by the expansion:

$$E \cong \frac{H_0}{A_0} + \frac{H_2}{A_0} - \frac{H_0 A_2}{A_0^3} \quad (3.10)$$

where the first term H_0/A_0 is of the zeroth order in T and may give the main term in the total energy of the molecule, and the second and third terms are of the order of T^2 and may be assumed as the correction for the first term.

§ 4. Details of the Energy Expression

The Hamiltonian of the entire system is taken as

$$\mathcal{H} = \sum_{\mu} h(\mu) + \sum_{(\mu\nu)} \frac{1}{r_{\mu\nu}} + \sum_{(XY)} \frac{Z_X Z_Y}{R_{XY}}, \quad (4.1)$$

where

$$h(\mu) = -\frac{1}{2} A(\mu) - \sum_X \frac{Z_X}{r_{X\mu}}.$$

$h(\mu)$ is the core operator which depends only on the coordinates of the μ th electron and the second and third terms in Eq. (4.1) give the repulsive Coulomb potentials between electrons and between nuclei, respectively. Then, we easily obtain the following expressions for the individual terms in the approximate formula (3.10) for the energy of the molecule. For the first term in Eq. (3.10), we obtain

$$\frac{H_0}{A_0} = \sum_{(ij)} H(ij) + \sum_{\{(ij)(kl)\}} A(ij, kl) + \sum_{(XY)} \frac{Z_X Z_Y}{R_{XY}}, \quad (4.2)$$

where

$$\left. \begin{aligned} H(ij) &= \frac{1}{1+S_{ij}^2} \{ I_{ii} + I_{jj} + 2S_{ij}I_{ij} + C_{ij} + K_{ij} \}^2, \\ A(ij, kl) &= \frac{1}{(1+S_{ij}^2)(1+S_{kl}^2)} \{ C_{ik} + C_{jk} + C_{il} + C_{jl} + 2S_{ij}(D_{ik,ij} + D_{il,ij}) \\ &\quad + 2S_{kl}(D_{ik,kl} + D_{jl,kl}) + 4S_{ij}S_{kl}N_{ij,kl} \} \end{aligned} \right\} \quad (4.3)$$

with

$$\left. \begin{aligned}
 I_{ij} &= (\phi_i | h | \phi_j) = \int \phi_i(1) h(1) \phi_j(1) dv_1, \\
 C_{ij} &= (\phi_i \phi_i; \phi_j \phi_j) = \iint \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_i(1) \phi_j(2) dv_1 dv_2, \\
 K_{ij} &= (\phi_i \phi_j; \phi_i \phi_j) = \iint \phi_i(2) \phi_j(1) \frac{1}{r_{12}} \phi_i(1) \phi_j(2) dv_1 dv_2, \\
 D_{k,ij} &= (\phi_k \phi_k; \phi_i \phi_j) = \iint \phi_k(1) \phi_i(2) \frac{1}{r_{12}} \phi_k(1) \phi_j(2) dv_1 dv_2, \\
 N_{ij,kl} &= (\phi_i \phi_j; \phi_k \phi_l) = \iint \phi_i(1) \phi_k(2) \frac{1}{r_{12}} \phi_j(1) \phi_l(2) dv_1 dv_2,
 \end{aligned} \right\} \quad (4.4)$$

$\sum_{(ij)}$ and $\sum_{\{(ij)(kl)\}}$ denote the summation over all the orbital pairs and of all pairs of orbital pairs, respectively. The second term in Eq. (3.10) is written as the following:

$$\frac{H_2}{A_0} = -\frac{1}{2} \sum_{\{(ij)(kl)\}} \{B(ij, kl) + A(ij, kl) (\sum''_{(pq)} H(pq) + \sum''_{\{(pq)(st)\}} A(pq, st))\} + \frac{A_2}{A_0} \sum_{(XY)} \frac{Z_X Z_Y}{R_{XY}} \quad (4.5)$$

with

$$\begin{aligned}
 B(ij, kl) &= \frac{1}{(1+S_{ij}^2)(1+S_{kl}^2)} \left[K_{ik} + K_{jk} + K_{il} + K_{jl} + 2S_{ij}(L_{kl,ij} + L_{l,ij}) \right. \\
 &\quad + 2S_{kl}(L_{i,kl} + L_{j,kl}) + 2S_{ij}S_{kl}(N_{ik,jl} + N_{il,jk}) \\
 &\quad + (T_{jk}^2 + T_{jl}^2 + 2S_{kl}T_{jk}T_{jl})\alpha_i + (T_{ik}^2 + T_{il}^2 + 2S_{kl}T_{ik}T_{il})\alpha_j \\
 &\quad + (T_{il}^2 + T_{jl}^2 + 2S_{ij}T_{il}T_{jl})\alpha_k + (T_{ik}^2 + T_{jk}^2 + 2S_{ij}T_{ik}T_{jk})\alpha_l \\
 &\quad + 2(T_{ik}T_{jk} + T_{il}T_{jl} + S_{kl}(T_{ik}T_{jl} + T_{il}T_{jk}))\beta_{ij} \\
 &\quad + 2(T_{ik}T_{il} + T_{jk}T_{jl} + S_{ij}(T_{ik}T_{jl} + T_{il}T_{jk}))\beta_{kl} \\
 &\quad + 2(T_{ik} + S_{ij}T_{jk} + S_{kl}T_{il} + S_{ij}S_{kl}T_{jl})\beta_{ik} \\
 &\quad + 2(T_{jk} + S_{ij}T_{ik} + S_{kl}T_{jl} + S_{ij}S_{kl}T_{il})\beta_{jk} \\
 &\quad + 2(T_{il} + S_{ij}T_{jl} + S_{kl}T_{ik} + S_{ij}S_{kl}T_{jk})\beta_{il} \\
 &\quad + 2(T_{jl} + S_{ij}T_{il} + S_{kl}T_{jk} + S_{ij}S_{kl}T_{ik})\beta_{jl} \\
 &\quad + T_{ji}^2 C_{ik} + T_{ik}^2 C_{jk} + T_{jk}^2 C_{il} + T_{ik}^2 C_{jl} + 2T_{il}T_{jl}D_{kl,ij} + 2T_{ik}T_{jk}D_{l,ij} \\
 &\quad + 2T_{jk}T_{jl}D_{i,kl} + 2T_{ik}T_{jl}D_{j,kl} + 2(T_{ik}T_{jl} + T_{il}T_{jk})N_{ij,kl} \\
 &\quad + 2(T_{ik} + S_{kl}T_{il})(D_{j,ik} + L_{j,ik}) + 2(T_{ik} + S_{ij}T_{jk})(D_{l,ik} + L_{l,ik}) \\
 &\quad + 2(T_{jk} + S_{kl}T_{jl})(D_{i,jk} + L_{i,jk}) + 2(T_{jk} + S_{ij}T_{ik})(D_{l,jk} + L_{l,jk}) \\
 &\quad + 2(T_{il} + S_{kl}T_{ik})(D_{j,il} + L_{j,il}) + 2(T_{il} + S_{ij}T_{jl})(D_{k,il} + L_{k,il}) \\
 &\quad \left. + 2(T_{jl} + S_{kl}T_{jk})(D_{i,jl} + L_{i,jl}) + 2(T_{jl} + S_{ij}T_{il})(D_{k,jl} + L_{k,jl}) \right], \quad (4.6)
 \end{aligned}$$

and

$$\begin{aligned}
 \alpha_i - I_{ii} + \sum''_{(pq)} \frac{1}{1+S_{pq}^2} (C_{ip} + C_{iq} + 2S_{pq}D_{i,pq}), \\
 \beta_{ij} = I_{ij} + \sum''_{(pq)} \frac{1}{1+S_{pq}^2} (D_{p,ij} + D_{q,ij} + 2S_{pq}N_{pq,ij}).
 \end{aligned}$$

where

$$L_{k,ij} = (\phi_k \phi_i; \phi_j \phi_k) = \iint \phi_k(1) \phi_i(2) \frac{1}{r_{12}} \phi_j(1) \phi_k(2) dv_1 dv_2$$

and $\sum''_{(pq)}$ denotes the summation over all the orbital pairs other than the two pairs (ij) and (kl) . We shall use the notation (ij) to refer to the orbital pair (ϕ_i, ϕ_j) and the corresponding bond. We assume the exchange integrals between unpaired orbitals as second order terms. By making use of Eqs. (3.7) and (4.2), the third term in Eq. (3.10) is expressed as

$$-\frac{\Delta_2 H_0}{\Delta_0^2} = \frac{1}{2} \sum_{\{(ij)(kl)\}} \Delta(ij, kl) \left[H(ij) + H(kl) + A(ij, kl) + \sum''_{(pq)} \{A(ij, pq) + A(kl, pq)\} \right] \\ + \frac{1}{2} \sum_{\{(ij)(kl)\}} \Delta(ij, kl) \{ \sum''_{(pq)} H(pq) + \sum''_{\{(pq)(st)\}} A(pq, st) \} - \frac{\Delta_2}{\Delta_0} \left(\sum_{(XY)} \frac{Z_X Z_Y}{R_{XY}} \right) \}. \quad (4.7)$$

The terms within the last two brackets in Eq. (4.7) give no contribution to the total energy due to the cancellation with the same terms in Eq. (4.5). Thus, the net contribution to the total energy from the quantities of order T^2 is

$$\frac{H_2}{\Delta_0} - \frac{\Delta_2 H_0}{\Delta_0^2} = \frac{1}{2} \sum_{\{(ij)(kl)\}} [\Delta(ij, kl) \{ H(ij) + H(kl) + A(ij, kl) \\ + \sum''_{(pq)} (A(ij, pq) + A(kl, pq)) \} - B(ij, kl)]. \quad (4.8)$$

It should be noted that Eq. (4.8) does not contain the quantity proportional to N^2 , if we assume the exponential decrease of the overlap integrals and the neutralization of the potentials due to the remoting atoms.

§ 5. Comparison with the Electron Pair Bond Theory

We shall rearrange the terms in the formulae given in the preceding section to compare with the description in the electron pair bond theory. The term H_0/Δ_0 of Eq. (4.2) involves the atomic energy terms, Coulomb terms and the exchange terms between the bonding electrons. If we consider that the expression

$$I_{ii} + \frac{1}{2} \sum_{i \neq j} \sum C_{ij} + \sum_{(XY)} \frac{Z_X Z_Y}{R_{XY}} \quad (5.1)$$

corresponds to the atomic energy terms and the Coulomb terms, we should interpret

$$J(ij) = \frac{1}{1 + S_{ij}^2} \left[K_{ij} + 2S_{ij} \left\{ I_{ij} + \sum'_{(kl)} \frac{1}{1 + S_{kl}^2} (D_{k,ij} + D_{l,ij} + 2S_{ij} N_{ij,kl}) \right\} \right. \\ \left. - S_{ij}^2 \{ I_{ii} + I_{jj} + C_{ij} + \sum'_{(kl)} (C_{ik} + C_{jk} + C_{il} + C_{jl}) \} \right] \\ + \frac{1}{2} \sum'_{(kl)} \frac{S_{ij} S_{kl}}{(1 + S_{ij}^2)(1 + S_{kl}^2)} \{ S_{ij} S_{kl} (C_{ik} + C_{jk} + C_{il} + C_{jl}) - 4N_{ij,kl} \} \quad (5.2)$$

as the exchange term between the bonding electrons which occupy the orbital pair (ϕ_i, ϕ_j) . Eq. (5.1) is equivalent to the usual definition in the electron pair bond theory, but we have to add the intra-atomic exchange integrals to Eq. (5.1) to obtain the sum of the atomic energies. Under such consideration Eq. (5.1) is expanded as

$$\sum_A E_A^* + \sum_{(AB)} Q(AB), \quad (5.3)$$

where E_A^* is the energy of a valence state of a constituent atom A and the summation extends over all atoms in the molecule. In the Heitler-London approximation we can easily obtain the following expression for E_A^* :

$$E_A^* = E_A^0 + \sum_a I_{aa}^A + \sum_{(aa')} (C_{aa'} - \frac{1}{2} K_{aa'}), \quad (5.4)$$

where

$$I_{aa}^A = (\phi_a | -\frac{1}{2}\Delta + V^A | \phi_a) \\ = \int \phi_a(1) [-\frac{1}{2}\Delta(1) + V^A(1)] \phi_a(1) dv_1,$$

and E_A^0 is the part of the atomic energy which depends only on the core electrons and V^A is the core potential for the valence electron which consists of the Hartree-Fock field due to the core electrons and the Coulomb potential due to the nucleus in the atom A . $Q(AB)$ corresponds to the Coulomb interaction energy between the two neutral atoms A and B :

$$Q(AB) = \sum_a V_{aa}^B + \sum_b V_{bb}^A + \sum_{(ab)} C_{ab} + V_{AB}, \quad (5.5)$$

where

$$V_{aa}^B = (\phi_a | V^B | \phi_a) = \int \phi_a(1) V^B(1) \phi_a(1) dv_1,$$

and V^B is the core potential of the atom B

just as V^A is that of the atom A . The summations $\sum_a$ and $\sum_b$ extend over the valence orbitals of the atoms A and B , respectively. V_{AB} represented the repulsive potential between the two atomic cores. $\sum_{(AB)}$ in Eq. (5.3) shows the summation over all the pairs of the constituent atoms. Now, we shall consider the correspondence of Eq. (5.2) with the usual definition. For doing this, the Mulliken approximation is assumed for the many center energy integrals according to the next two steps:

$$\left. \begin{aligned} 1. N_{ij,kl} &\cong \frac{1}{2} S_{kl} (D_{k,ij} + D_{l,ij}) \\ &\cong \frac{1}{4} S_{ij} S_{kl} (C_{ik} + C_{jk} + C_{il} + C_{jl}), \\ 2. V_{ij}^c + \sum_c D_{c,ij} \\ &\cong \frac{S_{ij}}{2} \{ (V_{ii}^c + \sum_c C_{ci}) + (V_{jj}^c + \sum_c C_{cj}) \} \end{aligned} \right\} \quad (5.6)$$

where $V_{ij}^c = (\phi_i | V^c | \phi_j)$ and V^c stands for the core potential of the atom C , and ϕ_i and ϕ_j are the valence orbitals belonging to the other atoms than the atom C . c denotes a valence orbitals of the atom C and $\sum_c$ represents the summation over all the valence orbitals of the atom C . Under the above assumption we get the expression of

$$J(ij) = \frac{1}{1+S_{ij}^2} [K_{ij} + 2S_{ij} \{ I_{ij}^{AB} + \sum_{a \neq i} D_{a,ij} + \sum_{b \neq j} D_{b,ij} \} - S_{ij}^2 \{ I_{ii}^{AB} + I_{jj}^{AB} + C_{ij} + \sum_{a \neq i} (C_{ai} + C_{aj}) + \sum_{b \neq j} (C_{bi} + C_{bj}) \}], \quad (5.7)$$

where

$$\begin{aligned} I_{ij}^{AB} &= (\phi_i | -\frac{1}{2} \Delta + V^A + V^B | \phi_j) \\ &= \int \phi_i(1) [-\frac{1}{2} \Delta(1) + V^A(1) + V^B(1)] \phi_j(1) dv_1. \end{aligned}$$

Further, if we assume that the valence orbital ϕ_i of the atom A is the eigenfunction of the equation

$$\{ -\frac{1}{2} \Delta + V^A + \sum_{a \neq i} (C_a - \frac{1}{2} K_a) \} \phi_i = \varepsilon_i^A \phi_i, \quad (5.8)$$

where $\sum_{a \neq i} (C_a - \frac{1}{2} K_a)$ indicates the Hartree-Fock type field due to the valence electrons other than the electron under consideration, and the summation is taken over all the valence orbitals of the atom A other than the orbital ϕ_i . ε_i^A is the quantity corresponding to the ionization potential of the valence orbital ϕ_i in the atom A . The analogous assumption has been made both in the π electron theory and in the electron pair bond theory. Adding the appropriate exchange type integrals

to Eq. (5.7), we obtain the expression

$$J(ij) = \frac{1}{1+S_{ij}^2} [K_{ij} + S_{ij} \{ V_{ij}^A + V_{ij}^B + \sum_{a \neq i} D_{a,ij} + \sum_{b \neq j} D_{b,ij} \} - S_{ij}^2 \{ V_{ii}^B + V_{jj}^A + C_{ij} + \sum_{b \neq j} C_{bi} + \sum_{a \neq i} C_{aj} \}], \quad (5.9)$$

under the above assumption. This expression for the exchange term between the bonding electrons is somewhat different from the usual definition in the electron pair bond theory.

The second order term $H_2/\Delta_0 - H_0 \Delta_2/\Delta_0^2$ expresses the contribution from the exchange terms between the non-bonding electrons. We cannot easily divide it into the individual exchange terms as usually done in the electron pair bond theory and must consider the exchange term between the two bonds (ij) and (kl) . According to Eq. (4.8) we take the following definition of the bond-bond exchange term:

$$\begin{aligned} J(ij, kl) &= B(ij, kl) - A(ij, kl) \{ H(ij) + H(kl) \\ &\quad + A(ij, kl) + \sum_{(pq)}'' (A(ij, pq) + A(kl, pq)) \}. \end{aligned} \quad (5.10)$$

If the two bonds (ij) and (kl) are adjacent and ϕ_j and ϕ_k are the valence orbitals of the same atom, we must add the appropriate exchange integrals to cancel out the terms considered in the derivation of Eqs. (5.3) and (5.9), since the corresponding terms are included in $J(ij, kl)$. These terms are

$$\left. \begin{aligned} &-K_{ik} \\ \text{or} & \\ &-\left(1 - \frac{S_{ij}^2}{1+S_{ij}^2} - \frac{S_{kl}^2}{1+S_{kl}^2} \right) K_{ik} \\ &-\frac{2S_{ij}}{1+S_{ij}^2} L_{k,ij} - \frac{2S_{kl}}{1+S_{kl}^2} L_{j,kl} \end{aligned} \right\} \quad (5.11)$$

according as we adopt (5.7) or (5.9) for the definition of $J(ij)$, respectively. We assume that $J(ij, kl)$ involves implicitly the correction term (5.11) in its definition. Now, the total energy of the system expressed to the second order in the overlap integral T is

$$\begin{aligned} E &= \sum_A E_A^* + \sum_{(AB)} Q(AB) + \sum_{(ij)} J(ij) \\ &\quad - \frac{1}{2} \sum_{\{(ij)(kl)\}} J(ij, kl). \end{aligned} \quad (5.12)$$

Thus, we must alter the definition of the exchange terms in the electron pair bond scheme, when we consider the non-orthogonality between the valence orbitals. The similar discussion was given by Nukasawa⁽⁴⁾ and Carr⁽⁵⁾. In their treatment, only one

atomic orbital was assumed for each atom and the magnitude of all the overlap integrals were assumed to be about the same, as Nukasawa considered the π electron system and Carr considered the system of electrons in the solid in connection with the theory of magnetism. In our system, each atom has several valence orbitals and the overlap integral between paired orbitals is distinguished from that between unpaired orbitals. Then, our definition for $J(ij)$ differs from that given by the above authors by a factor $1/(1+S_{ij}^2)$, as seen from Eq. (5.2), and this factor cannot be approximated with unity in our system. The definition for an exchange term in their papers is rather similar to that of $J(ij, kl)$, since a pair of orbitals for a chemical bond in our system corresponds to an atomic orbital in their system. These exchange terms originally contains the potential of the whole molecule, as Carr also pointed out. However, if we assume the approximate relation (5.6) for the molecular energy integrals, $J(ij)$ can be reduced to the form (5.7) and which depends only on the two atoms A and B . Under the equivalent assumption, it is easily found that $J(ij, kl)$ approximately depends only on the three of four atoms to which the orbitals ϕ_i, ϕ_j, ϕ_k and ϕ_l belong. The similar fact was also reported by Nukasawa.

§ 6. Discussion

Inglis⁽⁶⁾ firstly pointed out the difficulty due to the presence of the non-orthogonality inherent in the Heitler-London method. Against him, Vleck⁽⁷⁾ and Nukasawa⁽⁴⁾ discussed the contribution of the higher order permutations and obtained the conclusion that the expression of the total energy up to the second order of the overlaps in the Heitler-London method, which is equivalent to the electron pair bond theory, is rather a good approximation, although their discussions were based on the different approximate treatments. This result is, however, correct only in the case that the magnitude of the overlap integrals is small. In the saturated molecules which consist of only σ bonds, the magnitude of the overlap integral between paired orbitals S may be nearly equal to unity, but that between unpaired orbitals T is generally small. Thus, we must take S thoroughly into account, while we may stop with second order

of T . Eq. (3.10) is derived under the above consideration and may give a good approximation for the total energy of the molecule. In the preceding section, we showed that Eq. (3.10) gives the expression (5.12) in the electron pair bond scheme, if the exchange terms are interpreted appropriately. Therefore, it may be also a good approximation to use Eq. (5.12) for the calculation of the binding energy of the saturated molecule. Using Eq. (5.12) the binding energy $D(AB)$ of a bond $A-B$, which is bonded by the orbital pair (ϕ_i, ϕ_j) , may be defined as

$$D(AB) = Q(AB) + \sum_C \frac{1}{n_A + n_C} Q(AC) + \sum_D \frac{1}{n_B + n_D} Q(BD) + J(ij) - \frac{1}{4} \sum_{(kl) \neq (ij)}' J(ij, kl) + \left\{ \frac{1}{n_A} (E_A^* - E_A) + \frac{1}{n_B} (E_B^* - E_B) \right\}, \quad (6.1)$$

where n_A is the total number of the valence orbitals of the atom A . We have assumed for each atom to have the equivalent valence orbitals. The summations $\sum_C$ and $\sum_D$ extends over the atoms which do not link with the atom A and B , respectively. E_A and E_B are the energies of the ground states of the atoms A and B , respectively, and $E_A^* - E_A$ and $E_B^* - E_B$ are the promotional energies from the ground states to the valence states of the atoms A and B , respectively. In Eq. (6.1) the term $\sum_C 1/(n_A + n_C) Q(AC) + \sum_D 1/(n_B + n_D) Q(BD)$ may be small enough to be neglected, if the definition (5.5) of Q term is recalled. The value of $J(ij, kl)$ may be at least roughly proportional to the value of $A(ij, kl)$, and then we may safely neglect the exchange term between the bonds separated far from each other. In the first approximation it may be sufficient to assume that the summation $\sum_{(kl)}'$ in Eq. (6.1) is taken over the nearest neighbour bonds alone. If the exchange term between adjacent bonds is also small enough, the additive character of the binding energy in the saturated hydrocarbons is unlikely to be entirely accidental.

We next discussed the Mulliken approximation (5.6) which is used for the estimation of the many center energy integrals. If the orbital ϕ_i of the atom A is expanded in terms of the atomic orbitals of the atom B , we get

$$\phi_i = S_{ij} \phi_j + \sum_{b \neq j}' T_{ib} \phi_b, \quad (6.2)$$

where ϕ_b denotes an atomic orbitals of the atom B other than ϕ_j : The formulae (5.6) hold, if we retain only the first term in this expansion.⁽⁶⁾ If we substitute Eq. (6.2) into the expression of energy integral, we get

$$\left. \begin{aligned} 1. \quad N_{ij,kl} &= S_{ij} D_{j,kl} + \sum_{b \neq j}' T_{ib} N_{bj,kl}, \\ 2. \quad V_{ij}^{\sigma} + \sum_c D_{c,ij} &= S_{ij} (V_{jj}^{\sigma} + \sum_c C_{cj}) \\ &\quad + \sum_{b \neq j}' T_{ib} (V_{ib}^{\sigma} + \sum_c D_{c,ib}), \end{aligned} \right\} \quad (6.3)$$

where T_{ib} is the overlap integral between ϕ_i and ϕ_b , and its value is usually smaller than S_{ij} . Further the magnitudes of the energy integrals involved in the second term of the right hand side of Eq. (6.3) may be also small because of the orthogonality between ϕ_j and ϕ_b . Hence the approximate formulae (5.6) seems to be valid.

A calculation for the cohesive energy of diamond lattice has been carried out as an application of the present treatment and its detail will be published in the second article of this series. We shall discuss the contribution of the ionic terms to the binding energy of σ bond in the third article of this series.

There is no definite answer for the question whether a further approximation is necessary or not. The discussion on this problem will be given in the fourth article in the light of the molecular orbital method.

The author wishes to express his sincere thanks to Professor K. Niira for his incessant encouragement and also for his kind reading of the manuscript, and to professor E. Ishiguro for his valuable suggestions. This work is indebted to the Ministry of Education for its research grant.

References

- 1) C. A. Coulson: *Valence* (Oxford Univ. Press., 1951) 155.
- 2) H. H. Voge: J. Chem. Phys. **4** (1936) 581.
M. Kotani: *Research on the Molecular Structures* (Iwanami-shoten, 1953) 1. (in Japanese).
- 3) E. Aihara and K. Niira: J Phys. Soc. Japan **11** (1956) 1261.
- 4) K. Nukasawa: J. Chem. Phys. **20** (1952) 1983.
- 5) W. J. Carr, Jr.: Phys. Rev. **92** (1953) 28.
- 6) D. R. Inglis: Phys. Rev. **46** (1934) 135.
- 7) J. H. Van Vleck: Phys. Rev. **49** (1936) 232.
- 8) K. Rüdénberg: J. Chem. Phys. **19** (1951) 1433.

Intramolecular NMR Second Moment of the Polymer Chain

By Akira MIYAKE

*Department of Physics, Faculty of Liberal Arts and Science
Shizuoka University, Shizuoka*

(Received November 28, 1959)

The intramolecular NMR second moments of various amorphous vinyl-type polymers have been calculated in terms of the local regularity parameter z , the fraction of gauche-configuration bonds. These values of second moments at $z=0$ are to be compared with those calculated for crystalline polymers. The influence of foreign magnetic nuclei is negligibly small except for that of F nuclei to H -resonance and *vice versa*. The difference between isotactic and syndiotactic vinyl polymers has been shown. The error caused by omitting the contributions of farther distant nuclei than those where two $C-C$ bonds and two $C-H$ bonds intervene is estimated as less than a few percent of the total second moment for the amorphous polyethylene.

§ 1. Introduction

The NMR second moments in the rigid state of various polymers are obtained from the observed NMR absorption lines. For crystalline polymers, many successful comparisons between calculated values and observed ones of the second moment have given useful knowledges of the molecular structure and of the crystal structure.¹⁻⁵⁾ The powder average of theoretical NMR second moment has been given by Van Vleck⁶⁾ as

$$\Delta H_2^2 = \frac{3}{5} \frac{I(I+1)}{N} \left(\frac{\mu}{I} \right)^2 \sum_{j \neq k}^N \sum_{k=1}^N \langle r_{jk}^{-6} \rangle + \frac{4}{15} \sum_{j=1}^N \sum_f \frac{I_f(I_f+1)}{N} \left(\frac{\mu_f}{I_f} \right)^2 \langle r_{jf}^{-6} \rangle, \quad (1)$$

where N is the number of resonating nuclei, I their spin quantum number, μ their magnetic moment, r_{jk} the distance between the j th and the k th resonating nucleus, $\langle \rangle$ denotes the average value at the temperature T , the subscript f is concerned with the foreign magnetic nucleus.

In the solid polymer, we may usually consider only the secular contribution of nuclear magnetic interactions, because the spin-lattice relaxation time is relatively long. However if the non-secular contribution is especially to be taken into account, that is when the spin-lattice relaxation time is comparable with the spin-spin relaxation time, then instead of Eq. (1) we must use the equation given by the author and Chûjô,⁷⁾

$$\Delta H_2^2 = 2 \frac{I(I+1)}{N} \left(\frac{\mu}{I} \right)^2 \sum_{j \neq k}^N \sum_{k=1}^N \langle r_{jk}^{-6} \rangle + \frac{4}{3} \sum_{j=1}^N \sum_f \frac{I_f(I_f+1)}{N} \left(\frac{\mu_f}{I_f} \right)^2 \langle r_{jf}^{-6} \rangle. \quad (1')$$

It is worthy of notice, that we must take account of the effect of cutting off the long tails of absorption line on the observed second moment, when we speak of the motional narrowing of empirical second moment, which is not such a complete one as the theory predicts, and which varies usually in approximate parallel with the motional narrowing of line width.^{8,9)} On the other hand, the theoretical one, Eq. (1), is independent of the motional narrowing, as verified by Anderson¹⁰⁾ and by Kubo and Tomita,¹¹⁾ but is slightly dependent on the temperature through $\langle r_{jk}^{-6} \rangle$, which is concerned with the main subject of the present study.

Now for amorphous polymers, several values of the second moment observed in the rigid state have been reported,¹²⁾ but no theoretical ones accurately calculated are known, except for a supposition that these values in the amorphous region are scarcely different from those in the crystalline region because of the fact, that the observed value for the crystalline polymer of less than 100% degree of crystallization is in good accordance with the theoretical one for 100% degree of crystallization.

In order to clarify the difference between these values, we must calculate the NMR

second moment for the amorphous polymer, with the similar accuracy to that retained for the crystalline polymer. Unfortunately, the intermolecular contribution to the second moment is so difficult to calculate with a good accuracy for the amorphous polymer, that here we are content to examine only the intramolecular contribution, based on the statistics of trans-gauche transformation.¹³⁾

§ 2. Polyethylene-Type Chain

The author and Adachi¹³⁾ have shown, that the local regularity concerning the trans-gauche transformation of a linear chain is well described by a parameter, the fraction of gauche-configuration bonds z , which is equal to¹³⁾

$$z = \frac{2}{2 + \exp(\varepsilon/kT)} - \frac{2}{9} \exp(\varepsilon/kT) \left(\frac{fb}{kT} \right)^2, \quad (2)$$

where b is the skeletal $C-C$ bond length, the bond angle is taken as tetrahedral one, ε the energy difference between gauche- and

trans-configuration, f the stretching force imposed on both ends of the chain, k the Boltzmann constant, T the temperature.

Let the $C-H$ bond length be a , $\langle HCH$ and $\langle CCH$ be tetrahedral angles, H nuclei corresponding to G ($\varphi = \pi/3$) and G' -position ($\varphi = -\pi/3$) be denoted by H_i and H'_i , respectively, when C nucleus is in T -position ($\varphi = \pi$), the subscript i means the ordinal number of C nucleus to which H nuclei are bonded (cf. Fig. 1). Then the square of $H-H$ distance can be written as the quadratic form of a and b , the coefficients of which are given in Table I.

Using Table I, and summing up the contributions of as far as H_3 and H'_3 to H_1 and H'_1 in terms of the parameter z , we have intramolecular ΔH_2^2 of polyethylene-type polymer as

$$\begin{aligned} \Delta H_2^2 = & \frac{9}{8} a^2 \{ L_1 + 2(L_6 + L_7)(1-z) + (3L_6 + L_7)z \\ & + 2(L_2 + L_3)(1-z)^2 + 2(L_2 + L_3 + 2L_4)(1-z)z \\ & + \frac{1}{2}(L_2 + L_3 + 4L_4 + 2L_5)z^2 \}, \end{aligned} \quad (3)$$

where

$$\left. \begin{aligned} L_1 &= (\frac{8}{3}a^2)^{-3}, \quad L_2 = (\frac{8}{3}b^2)^{-3}, \quad L_3 = (\frac{8}{3}a^2 + \frac{8}{3}b^2)^{-3}, \\ L_4 &= (\frac{8}{3}a^2 + \frac{8}{3}ab + \frac{8}{3}b^2)^{-3}, \quad L_5 = (\frac{8}{3}a^2 + \frac{16}{3}ab + \frac{8}{3}b^2)^{-3}, \\ L_6 &= (\frac{4}{3}a^2 + \frac{4}{3}ab + b^2)^{-3}, \quad L_7 = (4a^2 + \frac{4}{3}ab + b^2)^{-3}. \end{aligned} \right\} \quad (4)$$

Assuming for the amorphous polyethylene, $-CH_2-CH_2-$, the following values:

Table I. Coefficients of the quadratic form of a and b , for the square of H-H distance.

φ_1	φ_2	a^2	ab	b^2	a^2	ab	b^2	a^2	ab	b^2	a^2	ab	b^2
					$(H_1H'_1)^2$ $\frac{8}{3}$	0	0						
		$(H_1H_2)^2$			$(H_1H'_2)^2$			$(H_1'H_2)^2$			$(H_1'H'_2)^2$		
T		4	4/3	1	4/3	4/3	1	4/3	4/3	1	4	4/3	1
G		4/3	4/3	1	4/3	4/3	1	4	4/3	1	4/3	4/3	1
G'		4/3	4/3	1	4	4/3	1	4/3	4/3	1	4/3	4/3	1
		$(H_1H_3)^2$			$(H_1H'_3)^2$			$(H_1'H_3)^2$			$(H_1'H'_3)^2$		
T	T	0	0	8/3	8/3	0	8/3	8/3	0	8/3	0	0	8/3
T	G	8/3	0	8/3	8/3	8/3	8/3	0	0	8/3	8/3	8/3	8/3
T	G'	8/3	8/3	8/3	0	0	8/3	8/3	8/3	8/3	8/3	0	8/3
G	T	8/3	8/3	8/3	8/3	8/3	8/3	0	0	8/3	8/3	0	8/3
G	G	8/3	8/3	8/3	8/3	16/3	8/3	8/3	0	8/3	8/3	8/3	8/3
G	G'	8/3	16/3	8/3	8/3	8/3	8/3	8/3	8/3	8/3	0	0	8/3
G'	T	8/3	0	8/3	0	0	8/3	8/3	8/3	8/3	8/3	8/3	8/3
G'	G	0	0	8/3	8/3	8/3	8/3	8/3	8/3	8/3	8/3	16/3	8/3
G'	G'	8/3	8/3	8/3	8/3	0	8/3	8/3	16/3	8/3	8/3	8/3	8/3

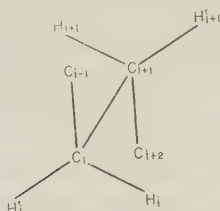


Fig. 1. Configuration of H_i and H'_i nuclei.

$$\left. \begin{aligned} \mu_H &= 2.793 \times 5.050 \times 10^{-24} \text{ erg/gauss}, \\ a &= 1.09 \text{ \AA}, \quad b = 1.54 \text{ \AA}, \end{aligned} \right\} \quad (5)$$

we obtain

$$\begin{aligned} \Delta H_2^2 &= 18.82 - 2.08z + 0.72z^2 \text{ gauss}^2 \\ &(-\text{CH}_2-\text{CH}_2-, \text{H-res.}). \end{aligned} \quad (6)$$

Similarly for the amorphous polytetrafluoroethylene, $-\text{CF}_2-\text{CF}_2-$, using, instead of Eq. (5), the following values:

$$\left. \begin{aligned} \mu_F &= 2.627 \times 5.050 \times 10^{-24} \text{ erg/gauss}, \\ a &= 1.33 \text{ \AA}, \quad b = 1.54 \text{ \AA}, \end{aligned} \right\} \quad (5')$$

we obtain

$$\begin{aligned} \Delta H_2^2 &= 7.86 - 1.46z + 0.63z^2 \text{ gauss}^2 \\ &(-\text{CF}_2-\text{CF}_2-, \text{F-res.}). \end{aligned} \quad (7)$$

Eqs. (6) and (7) are shown graphically in Fig. 2, where ΔH_2^2 decreases monotonously with the increase of z .

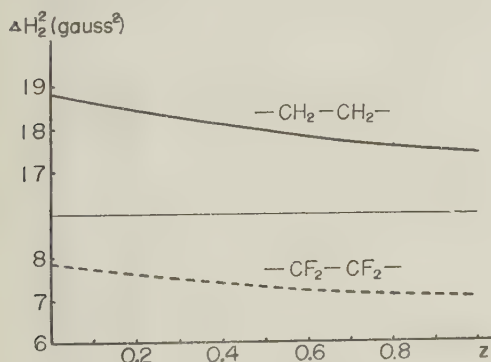


Fig. 2. ΔH_2^2 vs. z for polyethylene (H-resonance) and for polytetrafluoroethylene (F-resonance).

If we put $z=0$, then as for the polyethylene chain of all T -configurations Eq. (6) gives 18.82 gauss², which is to be compared with values for the crystalline one, 18.5 gauss² calculated by Andrew and Newman,¹⁾ 18.7 gauss² by McCall and Slichter¹⁾ and 17.8 gauss² by Nishioka *et al.*,³⁾ and as for the polytetrafluoroethylene chain Eq. (7) gives 7.86 gauss² to be compared with 7.66 gauss² by Smith,²⁾ 7.6 gauss² by Wilson and Pake²⁾, 7.5 gauss² by Slichter²⁾ and 9.23 gauss² by Nishioka *et al.*³⁾ A slight discrepancy among these values comes from trifling differences of bond lengths and bond angles adopted. We must care that the crystalline polytetrafluoroethylene has a helical structure, as reported by Bunn and Howells,¹⁴⁾ and so the calculated values based on the plane zig-zag structure are to be

modified.

§ 3. Polyvinyl Chloride-Type Chain

The stereospecificity of the polyvinyl chloride-type chain appears according as Cl nucleus resides in G - or G' -position when skeletal C nuclei are all in T -position. We must distinguish between the isotactic chain, in which all Cl nuclei reside in one side only of two positions, and the syndiotactic chain, in which Cl nuclei reside alternately in both positions.

Let the $C-Cl$ bond length be c , then the $H-Cl$ distance can be written as the quadratic form of a , b and c , the coefficients of which are given in Table II, where the super- and the subscript denote the similar meanings to the previous section.

Using Table II, we have

i) for the *isotactic* polyvinyl chloride chain

$$\begin{aligned} \Delta H_2^2 &= \frac{3}{5} \mu_H^2 \{ 2L_1 + 4(L_6 + L_7)(1-z) + 2(3L_6 + L_7)z \\ &\quad + 2(3L_2 + 2L_3)(1-z)^2 + 2(2L_2 + 3L_3 \\ &\quad + 5L_4)(1-z)z + \frac{1}{2}(3L_2 + 2L_3 + 10L_4 + 5L_5)z^2 \} \\ &\quad + \frac{4}{15} \mu_{Cl}^2 \{ M_1 + 2(M_2 + M_3)(1-z) + (3M_2 \\ &\quad + M_3)z + 2N_2(1-z)^2 + (2N_1 + N_3 \\ &\quad + N_4)(1-z)z + \frac{1}{2}(N_2 + N_3 + N_4 + N_5)z^2 \}, \end{aligned} \quad (8)$$

and ii) for the *syndiotactic* polyvinyl chloride chain

$$\begin{aligned} \Delta H_2^2 &= \frac{3}{5} \mu_H^2 \{ 2L_1 + 4(L_6 + L_7)(1-z) + 2(3L_6 + L_7)z \\ &\quad + 2(2L_2 + 3L_3)(1-z)^2 + 2(3L_2 + 2L_3 \\ &\quad + 5L_4)(1-z)z + \frac{1}{2}(2L_2 + 3L_3 + 10L_4 + 5L_5)z^2 \} \\ &\quad + \frac{4}{15} \mu_{Cl}^2 \{ M_1 + 2(M_2 + M_3)(1-z) + (3M_2 \\ &\quad + M_3)z + 2N_1(1-z)^2 + (2N_2 + N_3 \\ &\quad + N_4)(1-z)z + \frac{1}{2}(N_1 + N_3 + N_4 + N_5)z^2 \}, \end{aligned} \quad (8')$$

where

$$\left. \begin{aligned} M_1 &= (a^2 + c^2 + \frac{2}{3}ac)^{-3}, \\ M_2 &= (a^2 + b^2 + c^2 + \frac{2}{3}ab + \frac{2}{3}bc - \frac{2}{3}ac)^{-3}, \\ M_3 &= (a^2 + b^2 + c^2 + \frac{2}{3}ab + \frac{2}{3}bc + 2ac)^{-3}, \\ N_1 &= (a^2 + b^2 + c^2 - 2ac)^{-3}, \\ N_2 &= (a^2 + \frac{8}{3}b^2 + c^2 + \frac{2}{3}ac)^{-3}, \\ N_3 &= (a^2 + \frac{8}{3}b^2 + c^2 + \frac{8}{3}ab + \frac{2}{3}ac)^{-3}, \\ N_4 &= (a^2 + \frac{8}{3}b^2 + c^2 + \frac{8}{3}bc + \frac{2}{3}ac)^{-3}, \\ N_5 &= (a^2 + \frac{8}{3}b^2 + c^2 + \frac{8}{3}ab + \frac{8}{3}bc + \frac{2}{3}ac)^{-3}. \end{aligned} \right\} \quad (4')$$

Thus, using the values of

Table II. Coefficients of the quadratic form of a , b and c , for the square of $H-Cl$ distance

φ_1	φ_2	a^2	b^2	c^2	ab	bc	ac	a^2	b^2	c^2	ab	bc	ac
								$(H_1Cl_1')^2$ 1	0	1	0	0	2/3
		$(H_1Cl_2)^2$						$(H_1Cl_2')^2$					
T		1	1	1	2/3	2/3	2	1	1	1	2/3	2/3	-2/3
G		1	1	1	2/3	2/3	-2/3	1	1	1	2/3	2/3	-2/3
G'		1	1	1	2/3	2/3	-2/3	1	1	1	2/3	2/3	2
		$(H_1Cl_3)^2$						$(H_1Cl_3')^2$					
T	T	1	8/3	1	0	0	-2	1	8/3	1	0	0	2/3
T	G	1	8/3	1	0	0	2/3	1	8/3	1	0	8/3	2/3
T	G'	1	8/3	1	0	8/3	2/3	1	8/3	1	0	0	-2
G	T	1	8/3	1	8/3	0	2/3	1	8/3	1	8/3	0	2/3
G	G	1	8/3	1	8/3	0	2/3	1	8/3	1	8/3	8/3	2/3
G	G'	1	8/3	1	8/3	8/3	2/3	1	8/3	1	8/3	0	2/3
G'	T	1	8/3	1	0	0	2/3	1	8/3	1	0	0	-2
G'	G	1	8/3	1	0	0	-2	1	8/3	1	0	8/3	2/3
G'	G'	1	8/3	1	0	8/3	2/3	1	8/3	1	0	0	2/3
		$(H_1'Cl_1)^2$ 1	0	1	0	0	2/3						
		$(H_1'Cl_2)^2$						$(H_1'Cl_2')^2$					
T		1	1	1	2/3	2/3	-2/3	1	1	1	2/3	2/3	2
G		1	1	1	2/3	2/3	2	1	1	1	2/3	2/3	-2/3
G'		1	1	1	2/3	2/3	-2/3	1	1	1	2/3	2/3	-2/3
		$(H_1'Cl_3)^2$						$(H_1'Cl_3')^2$					
T	T	1	8/3	1	0	0	2/3	1	8/3	1	0	0	-2
T	G	1	8/3	1	0	0	-2	1	8/3	1	0	8/3	2/3
T	G'	1	8/3	1	0	8/3	2/3	1	8/3	1	0	0	2/3
G	T	1	8/3	1	0	0	-2	1	8/3	1	0	0	2/3
G	G	1	8/3	1	0	0	2/3	1	8/3	1	0	8/3	2/3
G	G'	1	8/3	1	0	8/3	2/3	1	8/3	1	0	0	-2
G'	T	1	8/3	1	8/3	0	2/3	1	8/3	1	8/3	0	2/3
G'	G	1	8/3	1	8/3	0	2/3	1	8/3	1	8/3	8/3	2/3
G'	G'	1	8/3	1	8/3	8/3	2/3	1	8/3	1	8/3	0	2/3

$$\left. \begin{aligned} \mu_{Cl} &= 0.7893 \times 5.050 \times 10^{-24} \text{ erg/gauss}^*) \\ c &= 1.74 \text{ \AA} \end{aligned} \right\} (5')$$

together with Eq. (5), we obtain for the amorphous polyvinyl chloride, $-CH_2-CHCl-$,

$$\begin{aligned} \Delta H_2^2 &= 13.47 - 2.89z + 1.34z^2 + (0.06 \\ &\quad + 0.01z - 0.02z^2) \text{ gauss}^2 \\ &\quad (\text{iso. } -CH_2-CHCl-, H\text{-res.}) \end{aligned} \quad (9)$$

and

$$\begin{aligned} \Delta H_2^2 &= 12.81 - 0.90z - 0.16z^2 \\ &\quad + (0.08 - 0.05z + 0.03z^2) \text{ gauss}^2 \\ &\quad (\text{syn. } -CH_2-CHCl-, H\text{-res.}), \end{aligned} \quad (9')$$

* This value is the root mean square of the magnetic moments for ^{35}Cl (75.4%) and ^{37}Cl (24.6%).

where those terms within the brackets express the contribution of Cl nuclei to the H-resonance. We can realize that those contributions are less than 1% and that the difference of stereospecificity, which affects ΔH_2^2 by a few percent as a whole, appears in the contributions of H nuclei rather than those of Cl nuclei.

Similarly, using Eqs. (5') and (5''), for the amorphous polytrifluoromonochloroethylene we have

$$\begin{aligned} \Delta H_2^2 &= 6.08 - 2.88z + 1.29z^2 \\ &\quad + (0.04 + 0.03z - 0.03z^2) \text{ gauss}^2 \\ &\quad (\text{iso. } -CF_2-CFCl-, F\text{-res.}) \end{aligned} \quad (10)$$

and

$$\begin{aligned}\Delta H_2^2 = & 5.40 - 0.84z - 0.23z^2 \\ & + (0.07 - 0.05z + 0.03z^2) \text{ gauss}^2 \\ & (\text{syn. } -\text{CF}_2-\text{CFCl}-, \text{F-res.}). \quad (10')\end{aligned}$$

In Fig. 3, Eqs. (9), (9'), (10) and (10') are shown graphically, and we can see the difference between isotactic and syndiotactic disappears at $z=2/3$, where T-, G- and G'-position are equally weighted. The values at $z=0$ in Eqs. (9) and (9') are to be compared with 12.7 gauss² (iso.) and 12.1 gauss² (syn.) calculated by Nishioka *et al.*³⁾ and 12.7 gauss² by Odajima *et al.*¹⁵⁾ for the crystalline polyvinyl chloride. And those in Eqs. (10) and (10') are to be compared with 7.4 gauss² (iso.) and 6.4 gauss² (syn.) by Nishioka *et al.*³⁾ for the crystalline polytrifluoromonoethylethylene.

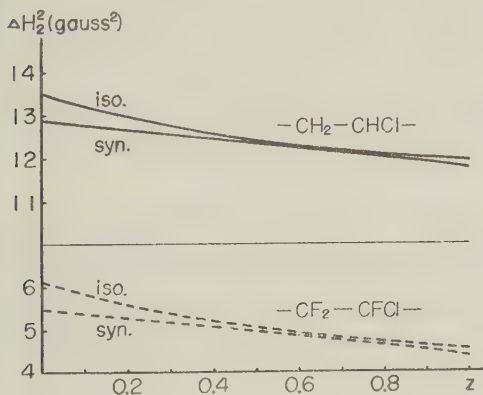


Fig. 3. ΔH_2^2 vs. z for polyvinyl chloride (H-resonance) and for polytrifluoromonoethylethylene (F-resonance).

§4. Fluorine Derivatives of Polyethylene Chain

For the amorphous polyvinyl fluoride, $-\text{CH}_2-\text{CHF}-$, using the values of

$$\left. \begin{aligned}\mu_{\text{H}} &= 2.793 \times 5.050 \times 10^{-24} \text{ erg/gauss}, \\ \mu_{\text{F}} &= 2.627 \times 5.050 \times 10^{-24} \text{ erg/gauss}, \\ a &= 1.09 \text{ \AA}, \quad b = 1.54 \text{ \AA}, \quad c = 1.33 \text{ \AA},\end{aligned} \right\} (5''')$$

we obtain as ΔH_2^2 of H-resonance, similarly to Eqs. (9) and (9'),

$$\begin{aligned}\Delta H_2^2 = & 13.47 - 2.89z + 1.34z^2 \\ & + (1.24 + 0.32z - 0.26z^2) \text{ gauss}^2 \\ & (\text{iso. } -\text{CH}_2-\text{CHF}-, \text{H-res.}) \quad (11)\end{aligned}$$

and

$$\begin{aligned}\Delta H_2^2 = & 12.81 - 0.90z - 0.16z^2 \\ & + (1.51 - 0.50z + 0.36z^2) \text{ gauss}^2 \\ & (\text{syn. } -\text{CH}_2-\text{CHF}-, \text{H-res.}), \quad (11')\end{aligned}$$

where the contributions of F nuclei within the brackets are appreciable, in contrast to Eqs. (9) and (9'), because the magnetic moment of F nucleus, is comparable to one of H nucleus, while that of Cl nucleus is much smaller.

As for ΔH_2^2 of F-resonance, by means of Eq. (5''') and the following equations:

i) for the isotactic polyvinyl fluoride

$$\begin{aligned}\Delta H_2^2 = & \frac{4}{5} \mu_{\text{H}}^2 \{ M_1 + 2(M_2 + M_3)(1-z) + (3M_2 + M_3)z \\ & + 2N_2(1-z)^2 + (2N_1 + N_3 + N_4)(1-z)z \\ & + \frac{1}{2}(N_2 + N_3 + N_4 + N_5)z^2 \} \\ & + \frac{9}{5} \mu_{\text{F}}^2 \{ 2L_2(1-z)^2 + 2(L_3' + L_4')(1-z)z \\ & + \frac{1}{2}(L_2 + 2L_4' + L_5')z^2 \}, \quad (12)\end{aligned}$$

and ii) for the syndiotactic polyvinyl fluoride

$$\begin{aligned}\Delta H_2^2 = & \frac{4}{5} \mu_{\text{H}}^2 \{ M_1 + 2(M_2 + M_3)(1-z) + (3M_2 + M_3)z \\ & + 2N_1(1-z)^2 + (2N_2 + N_3 + N_4)(1-z)z \\ & + \frac{1}{2}(N_1 + N_3 + N_4 + N_5)z^2 \} \\ & + \frac{9}{5} \mu_{\text{F}}^2 \{ 2L_3'(1-z)^2 + 2(L_2 + L_4')(1-z)z \\ & + \frac{1}{2}(L_3' + 2L_4' + L_5')z^2 \}, \quad (12')\end{aligned}$$

where

$$\begin{aligned}L_3' &= (\frac{8}{3}b^2 + \frac{8}{3}c^2)^{-3}, \quad L_4' = (\frac{8}{3}b^2 + \frac{8}{3}bc + \frac{8}{3}c^2)^{-3}, \\ L_5' &= (\frac{8}{3}b^2 + \frac{16}{3}bc + \frac{8}{3}c^2)^{-3}, \quad (4''')\end{aligned}$$

we obtain

$$\begin{aligned}\Delta H_2^2 = & 4.18 + 1.08z - 0.88z^2 \\ & + (2.50 - 4.39z + 2.60z^2) \text{ gauss}^2 \\ & (\text{iso. } -\text{CH}_2-\text{CHF}-, \text{F-res.}) \quad (13)\end{aligned}$$

and

$$\begin{aligned}\Delta H_2^2 = & 5.10 - 1.68z + 1.19z^2 \\ & + (0.47 + 1.70z - 1.97z^2) \text{ gauss}^2 \\ & (\text{syn. } -\text{CH}_2-\text{CHF}-, \text{F-res.}), \quad (13')\end{aligned}$$

where the terms within the brackets express the contributions of H nuclei.

Similarly, for the amorphous polytrifluoroethylene, $-\text{CF}_2-\text{CFH}-$, the counter-polymer of polyvinyl fluoride, we have for F-resonance

$$\begin{aligned}\Delta H_2^2 = & 6.08 - 2.88z + 1.29z^2 \\ & + (1.40 + 0.35z - 0.29z^2) \text{ gauss}^2 \\ & (\text{iso. } -\text{CF}_2-\text{CFH}-, \text{F-res.}), \quad (14)\end{aligned}$$

$$\begin{aligned}\Delta H_2^2 = & 5.40 - 0.84z - 0.23z^2 \\ & + (1.71 - 0.57z + 0.40z^2) \text{ gauss}^2 \\ & (\text{syn. } -\text{CF}_2-\text{CFH}-, \text{F-res.}), \quad (14')\end{aligned}$$

and for H -resonance,

$$\begin{aligned} \Delta H_2^2 = & 3.70 + 0.96z - 0.79z^2 \\ & + (2.83 - 4.97z + 2.94z^2) \text{ gauss}^2 \\ & (\text{iso. } -CF_2-CFH-, H\text{-res.}), \end{aligned} \quad (15)$$

$$\begin{aligned} \Delta H_2^2 = & 4.52 - 1.50z + 1.06z^2 \\ & + (0.53 + 1.93z - 2.23 + z^2) \text{ gauss}^2 \\ & (\text{syn. } -CF_2-CFH-, H\text{-res.}). \end{aligned} \quad (15')$$

Now, for the amorphous polyvinylidene fluoride, $-CH_2-CF_2-$, by means of Eq. (5'') and the equation:

$$\begin{aligned} \Delta H_2^2 = & \frac{9}{8}\mu_H^2\{L_1 + 2(L_2 + L_3)(1-z)^2 + 2(L_2 + L_3 \\ & + 2L_4)(1-z)z + \frac{1}{2}(L_2 + L_3 + 4L_4 + 2L_5)z^2\} \\ & + \frac{4}{8}\mu_F^2\{2(M_2 + M_3)(1-z) + (3M_2 + M_3)z\}, \end{aligned} \quad (16)$$

we have for H -resonance

$$\begin{aligned} \Delta H_2^2 = & 14.93 - 3.41z + 0.98z^2 \\ & + (1.11 + 0.32z) \text{ gauss}^2 \\ & (-CH_2-CF_2-, H\text{-res.}) \end{aligned} \quad (17)$$

and similarly for F -resonance

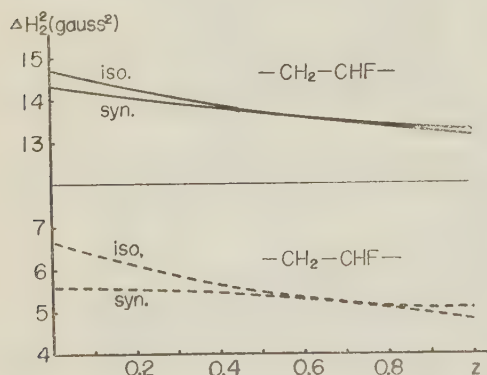


Fig. 4. ΔH_2^2 vs. z for polyvinyl fluoride, H -resonance (full curves) and F -resonance (dotted curves).

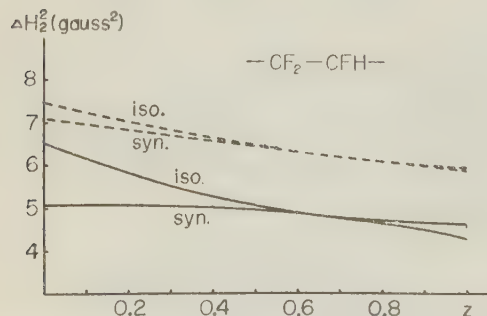


Fig. 5. ΔH_2^2 vs. z for polytrifluoroethylene, H -resonance (full curves) and F -resonance (dotted curves).

$$\begin{aligned} \Delta H_2^2 = & 5.99 - 2.69z + 0.56z^2 \\ & + (1.25 + 0.37z) \text{ gauss}^2 \\ & (-CH_2-CF_2-, F\text{-res.}). \end{aligned} \quad (18)$$

Eqs. (11), (11'), (13) and (13') are shown graphically in Fig. 4, Eqs. (14), (14'), (15) and (15') are in Fig. 5, and Eqs. (17) and (18) are in Fig. 6, where the values at $z=0$ are to be compared with those calculated by Slichter²⁾ for the crystalline polymers, 14.3 gauss² (H -res.) and 5.8 gauss² (F -res.) for polyvinyl fluoride, 5.9 gauss² (H -res.) and 6.8 gauss² (F -res.) for polytrifluoroethylene and 15.7 gauss² (H -res.) and 7.1 gauss² (F -res.) for polyvinylidene fluoride.

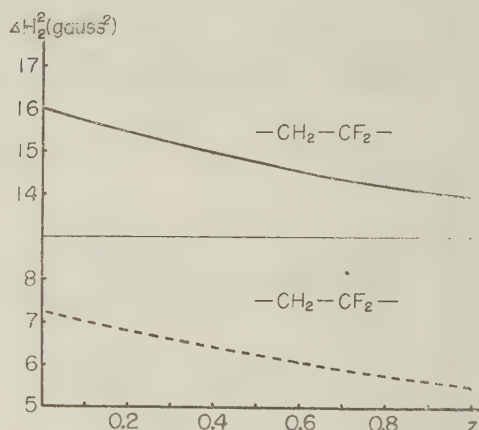


Fig. 6. ΔH_2^2 vs. z for polyvinylidene fluoride, H -resonance (full curves) and F -resonance (dotted curves).

§ 5. Discussions

Let us estimate the error caused by omitting the contributions of farther distant magnetic nuclei from the calculations given above.

For instance, in the case of polyethylene, the contributions of those nuclei distant farther than H_3 and H_3' to H_1 and H_1' are neglected. Suppose the distance between H_1 or H_1' and H_4 or H_4' is equivalent to the distance of 4 skeletal bonds, as the former distance involves 2 $C-H$ bonds and 3 $C-C$ bonds, and so on. The mean square distance of n skeletal bonds is given by¹⁶⁾

$$\langle r_n^2 \rangle = nb^2 \frac{2}{3} \{1 + 2 \exp(-\epsilon/kT)\} \geq 2nb^2, \quad (19)$$

provided the bond angles are tetrahedral ones and $\epsilon \geq 0$. Considering the excluded volume effect, we may take approximately

$$\langle r_n^{-6} \rangle \cong \langle r_n^2 \rangle^{-3},$$

then the error of ΔH_2^2 for amorphous polyethylene is calculated as

$$\begin{aligned} \delta \Delta H_2^2 &\cong \frac{9}{5} \mu^2 \sum_{n=4}^{\infty} 2 \times 2 \langle r_n^2 \rangle^{-3} \\ &\leq \frac{9 \mu_H^2}{10 b^2} \sum_{n=4}^{\infty} 1/n^3 = 0.53 \text{ gauss}^2, \end{aligned} \quad (20)$$

which is less than a few percent of total ΔH_2^2 . In other cases we can expect the error of the similar percentage, which is less than the difference in ΔH_2 due to the stereospecificity shown in §§ 4 and 5.

We must remark that, as referred to in § 1, in order to compare the calculated second moment with the observed one, one must take account of the intermolecular contribution, which is untouched in the present study, in addition to the intramolecular contribution examined in the present article, and, sorry to say, the intermolecular one is much less accurately known for the amorphous polymer than for the crystalline one.

The author is grateful to Mr. R. Chûjô for good assistance in the present work.

References

- 1) E. R. Andrew: *J. Chem. Phys.* **18** (1950) 607. R. Newman: *ibid.* **18** (1950) 1303. D. W. McCall and W. P. Slichter: *J. Polymer Sci.* **26** (1957) 171.
- 2) J. A. S. Smith: *Discussions Faraday Soc.* No. 19, (1955) 207. C. W. Wilson, III and G. E. Pake: *J. Chem. Phys.* **27** (1957) 115. W. P. Slichter: *J. Polymer Sci.* **24** (1957) 173.
- 3) A. Nishioka, H. Komatsu and Y. Kakiuchi: *J. Phys. Soc. Japan* **12** (1957) 283. A. Nishioka: *J. Polymer Sci.* **37** (1959) 163.
- 4) W. P. Slichter: *J. Appl. Phys.* **26** (1955) 1099; *J. Polymer Sci.* **35** (1958) 77.
- 5) R. Land, R. E. Richards and I. M. Ward: *Trans. Faraday Soc.* **55** (1959) 225.
- 6) J. H. Van Vleck: *Phys. Rev.* **74** (1948) 1168.
- 7) A. Miyake and R. Chûjô: *Busseiron-Kenkyû Ser. II*, **2** (1957) 769; *J. Phys. Soc. Japan* **15** (1960) 198.
- 8) A. Miyake: *Kôbunshi-Kagaku* **16** (1959) 40.
- 9) E. R. Andrew and R. A. Newing: *Proc. Phys. Soc. London* **72** (1958) 959.
- 10) P. W. Anderson: *J. Phys. Soc. Japan* **9** (1954) 316.
- 11) R. Kubo and K. Tomita: *J. Phys. Soc. Japan* **9** (1954) 888.
- 12) H. S. Gutowsky and L. H. Meyer: *J. Chem. Phys.* **21** (1953) 2122. J. G. Powles: *J. Polymer Sci.* **22** (1956) 79; *Proc. Phys. Soc. London B*, **69** (1956) 281.
- 13) A. Miyake and H. Adachi: *Busseiron-Kenkyû Ser. II*, **5** (1959) 257; *J. Polymer Sci.* (in press).
- 14) C. W. Bunn and E. R. Howells: *Nature* **174** (1954) 549.
- 15) A. Odajima, J. Sohma and M. Koike: *J. Phys. Soc. Japan* **12** (1957) 272.
- 16) S. Oka: *Proc. Phys.-Math. Soc. Japan* **24** (1942) 657. W. J. Taylor: *J. Chem. Phys.* **15** (1947) 412; *ibid.* **16** (1948) 257. H. Kuhn: *ibid.* **15** (1947) 843. M. H. Benoit: *J. Chim. Phys.* **44** (1947) 18. R. Kubo: *J. Phys. Soc. Japan* **3** (1948) 119; *ibid.* **4** (1949) 319.

Zeeman Quadrupole Spectra in *p*-dichlorobenzene and *p*-chlorobenzoic Acid

By Shizuko OGAWA and Kikuo OHI

Department of Physics, Ochanomizu University

(Received February 6, 1960)

Zeeman effects of nuclear quadrupole resonance of *p*-dichlorobenzene and *p*-chlorobenzoic acid were studied. For *p*-chlorobenzoic acid only one C-Cl bond direction was observed. The molecular orientation against the crystal *c*-axis was obtained by the *x*-ray measurement. The asymmetry parameter was determined from the Zeeman effect to be 8%. For *p*-dichlorobenzene, the molecular orientation of the α phase to the β phase was studied. In most crystals examined the orientation in two phases is defined respectively. However, there is no relation in two phases. The orientation may be restricted by dislocations which exist previously in single crystal. The obtained value of the asymmetry parameter is 6% which is smaller than Dean's.

§ 1. Introduction

In the case of chlorine nucleus, having nuclear spin $I=3/2$ a single quadrupole resonance line corresponding to transition $m_z=\pm 1/2 \leftrightarrow \pm 3/2$ is observed. From the resonance frequency and the Zeeman effect of the resonance line, informations about the molecular structure are obtained. For a chlorine nucleus in C-Cl bond the principal axis of the electric field gradient tensor q_{zz} considered to lie upon the bond direction. Three principal components of the field gradient tensor give a field asymmetry parameter.

Nuclear quadrupole resonance spectra and Zeeman effect of *p*-dichlorobenzene were studied by Dean^{1/2}). It has two phases which are sometimes observed simultaneously at the temperatures near the transition point of 32°C. The resonance frequency of high temperature phase (β) is lower about 23 kc than that of low temperature phase (α). The structure of the α phase is monoclinic and the unit cell contains two molecules. The β phase was studied also by Dean and Lutz³). The crystal structure is triclinic and the unit cell has only one molecule. Lutz's Zeeman data showed that the C1-C1 direction in the β phase could not be related to the two C1-C1 directions in the α phase. We also investigated the relation of the C1-C1 directions in two phases. Each single crystal was made to change its phase repeatedly to observe the Zeeman effect for every

phase.

Zeeman effect was also studied for a single crystal of *p*-chlorobenzoic acid. Nuclear quadrupole resonance line was observed by Allen⁴). Zeeman effect was not studied.

§ 2. Procedure of Experiment and Analysis

a) Single crystals

A glass cylinder of 30 mm in diameter and 50 mm long tapered to a capillary about a few cm long was sealed after the powdered sample was filled. The sample was melted in a furnace and was descended slowly to a position cooled with a water bath⁵). *p*-dichlorobenzene has the melting point of 57°C. Temperature of the furnace was 80°C and the temperature gradient was 7°C/cm. The speed of descending the ampule was 1 cm/h. Usually colourless transparent crystal of the α phase was easily obtained. In summer, however, the crystal was several times in the β phase. About thirty single crystals were made.

p-chlorobenzoic acid has the melting point of 243°C and sublimes. A sealed ampule was suspended with a copper wire and the sample was melted in a furnace at a temperature about 350°C. The furnace has a temperature gradient of 10°C/cm and a descending speed of 3 mm/h. Higher rates of descending speed could not make a single crystal adequately. In stead of the water bath above mentioned a oil bath was used to keep a constant temperature plane. The surface of oil was 120°C. The sample segre-

gated impurities at the glass wall and small thin crystals were deposited over the crystal surface. The ampule was carefully cut at the end of the sealed position to prevent the explosion account of the accumulated inner pressure of decomposed gas. When a crystallization was repeated three times after the removal of impurities at every time, the resonance signal on the oscilloscope was improved surprisingly.

b) Apparatus

An LC-tuned superregenerative oscillator was used to observe the lines⁶⁾. The resonance frequencies are about 3.42 Mc at room temperature. Magnetic field for Zeeman study was provided by Helmholtz coils which had a mean diameter of 20cm and mounted on a rotating plate. The axis of the coils was rotated about a vertical axis. Field strength was 100 gauss usually and was varied up to 500 gauss for detail survey. The direction of the magnetic field to the rf field was indicated by rotating angles with an accuracy of 18'. The crystal was rotated about the axis of the rf field. The accuracy of the rotating angles was 12'.

In order to study the phase relation of *p*-dichlorobenzene, a crystal was warmed in a box with the resonating oscillator coil and the magnet. Zeeman study was carried out under this condition. The magnet was controlled from outside of the box and the angle was read through the window. When the Zeeman pattern on oscilloscope changed under the same orientation of the sample and the magnet, the occurrence of the phase transition was recognized. For the purpose of obtaining the angles from the Zeeman study of α phase against that of β phase accurately, it is preferable to observe the pattern of both phase without taking off the sample from the oscillator coil. The time required for this process was longer than several hours. Because of the different crystal densities for two phases, the crystal was sometimes distorted by strains when the phase transition occurred. In these cases the component lines of the Zeeman pattern became so broad that the detailed analysis was impossible. Thus the process of changing temperature through several hours did not sufficient for our purpose. It is better to have several days without any undesirable

strains. Therefore the sample was taken off from the oscillator coil after analyzing the patterns of one phase and put into a thermostat about four days at the temperatures of 35°C and 10°C for change from α to β or reverse, respectively.

c) Zeeman effect

The energy levels of pure quadrupole interaction in a crystal for nuclear spin $I=3/2$;

$$\begin{aligned} E_{m_z=\pm 1/2} &= -\frac{eQq_{zz}}{4} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \\ E_{m_z=\pm 3/2} &= -\frac{eQq_{zz}}{3} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \end{aligned} \quad (1)$$

where $\eta = |q_{xx} - q_{yy}|/q_{zz}$, is an asymmetry parameter. When a static magnetic field is applied, above two degenerate levels split into four, in which the levels corresponding to $m_z = \pm 1/2$ are mixed. Single resonance line thus splits into four. The splitting is a function of the angle between the direction of the magnetic field and the axis of the field gradient tensor. When the orientation of the magnetic field satisfies the following relation

$$\sin^2 \theta = 1/(3 - \eta \cos 2\varphi), \quad (2)$$

the inner components coalesce to a single line. Where θ and φ show polar coordinates of the applied magnetic field referred to the principal axis system of the field gradient tensor⁷⁾. When $\eta=0$, the trace of this orientation produces a locus of $\theta=54^\circ 44'$. The direction of the center of this locus may be considered to lie upon the *z*-axis of the field gradient tensor. If the asymmetry exists, η is determined by the following relation;

$$\eta = \frac{3(\sin^2 \theta_{min} - \sin^2 \theta_{max})}{(\sin^2 \theta_{min} + \sin^2 \theta_{max})}. \quad (3)$$

The field gradient tensor axes of q_{xx} and q_{yy} are determined from the directions of θ_{min} and θ_{max} .

§ 3. Results

1) *p*-dichlorobenzene

One of the results of Zeeman effect for the repeated phase change on one crystal is shown in Fig. 1. In this figure relative orientation of the two phases is indicated. In Fig. 1 (b) the *x*-axis represents the plane which contains two C1-C1 directions of molecules in the α phase. The origin corresponds

to the crystal b -axis bisecting the angle composed of the two C1-C1 directions. The dot shows the position of the molecule in the α phase, and the bar indicates the benzene plane. The circle with bar shows the molecular orientation of the β phase against the last orientation of the α phase. It is recognized from this figure that in the repetition of the phase transition, the β phase usually retransforms to have nearly the same molecular orientation against the α phase. This orientation, however, shows a small disorder which can not be interpreted as the experimental error. The similar results were obtained from other crystals except having the different orientations between the two phases.

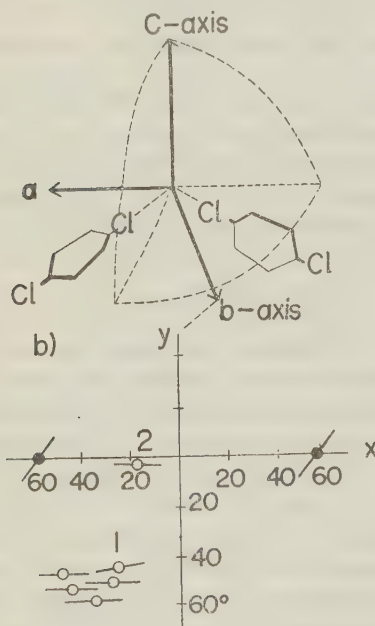


Fig. 1. a) Molecular orientation of p -dichlorobenzene for α phase. b) An example of molecular orientations in the β phase against to that in α phase. X-axis show the plane contained two C-Cl directions in the α phase. The bar shows a benzene plane. The group of bars (1) shows the orientations of the β phase in one crystal resulted from a repeated phase change experiments. The bar (2) shows one of the orientation of the β phase in an other crystal.

One example is indicated with bar 2 in Fig. 1 (b). In a few cases above relation between the two phases could not be found even in one crystal. The relative orientation of the phases in each crystal was not affected by annealing at 50°C for a week.

From the present results it is concluded that there are originally no universal relations between the molecular orientations of the two phases as observed by Lutz³⁾. However, in an individual crystal there seem to exist some causes to make the phase transition occur in the same way in every repetition. One of the causes may be the effect of the macroscopic structure of the glass ampule. This was, however, easily discarded since the crystal which was cut out to a different form showed the same relative orientation of the two phases as that in the ampule. It is likely that the dislocation in a crystal is one of the fundamental causes. The above phenomena suggest that in the repetition of the phase transition or in the annealing, the dislocations which initiate the phase transition remain unchanged as produced at the initial solidification.

2) p -chlorobenzoic acid

The single crystal used in this experiment was cut out through cleavages from a crystal produced in a glass cylinder. The crystal used for Zeeman study was 20mm long and 5×9mm² in square. It elongated along the cylinder axis. The crystal was mounted as the crystal axis being parallel to the rf field. The crystal structure was studied by J. Joussoint with x -ray analysis⁸⁾. It is a triclinic the three angles are $\alpha=91^\circ38'$, $\beta=95^\circ18'$ and $\gamma=92^\circ44'$, and lengths of a unit cell are $a=14.36$, $b=6.28$ and $c=3.85$ KX. The molecule is placed almost parallel to the plane (111) and the C1-COOH axis lie in the plane bisector of $(001)\wedge(100)$. There are two molecules in a unit cell and their C1-COOH axes situate antiparallel to each other. The plane of the benzene ring has an angle of 20° with (001).

Zeeman effect was studied in tracing the locus of the triplet pattern. From the analysis of the locus only one bonding direction was obtained. In Zeeman study of pure quadrupole resonance the difference of two above mentioned antiparallel molecules in a unit cell can not be obtained separately. The benzene plane was determined by the analysis of the triplet locus. The crystal axis of this sample was determined by the Laue pattern. The axis parallel to the glass cylinder was known to be the c -axis. The results are summarized in Table I. The er-

Table I.

	present experiment	x-ray
The angle between <i>c</i> -axis and C-Cl direction.	78° ± 5°	74°
The angle between <i>c</i> -axis and normal of the benzene plane	18° ± 10°	20°

Table II.

Molecule	η (%)	C=Cl+(%)	C+ Cl-(%)
<i>p</i> -Cl Φ COOH	8 ± 3	2.66 ± 1	20 ± 1
<i>p</i> -Cl ₂ Φ , α and β	6 ± 2	1.66 ± 0.7	20.9 ± 0.7
<i>p</i> -Cl ₂ Φ , Dean	8 ± 2	2.26 ± 0.7	20.4 ± 0.7

ror was estimated from the geometrical arrangement of the sample axis taken as parallel to a horizontal plane contains another source of error which results from the ambiguity to determine the direction of q_{xx} . The data calculated from the x-ray analysis by J. Joussoint are also shown in this Table.

3) *Bond characters*

Asymmetry parameters of these compounds were derived from the deviated values of the triplet locus. Fig. 2 shows one example in the case of *p*-dichlorobenzene.

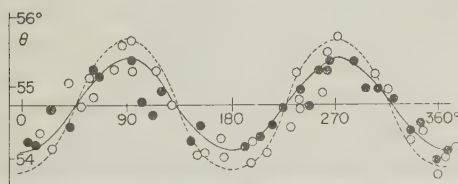


Fig. 2. One example for deviations of zerosplitting locus in paradichlorobenzene.

• α
 ○ β
 — $\eta=5\%$
 --- $\eta=7\%$

The ordinate is an angle measured from the center of the locus. The abscissa is the latitude about the direction of this center. In this figure solid lines show the calculated curves of η as 5% and 7%. The results of the two phases are plotted in the same scales. Since the intermolecular interaction is considered to be small for both phase, the same value of η of 6% is taken. Dean obtained the value of η for the α phase as 8%. From Fig. 2 the present value does not show a good consistency with Dean's.

The character of C-Cl bond consists mainly of covalent bond. Double bond and ionic bond characters are also possible. These bondings are α and π bonds, the fractions of which are a and b , respectively. It is assumed that α bond is s-p hybridized orbit and π bond is a pure p orbit. The numbers of unbalanced p electrons and η are given from the following relations⁹⁾¹⁰⁾

$$\begin{aligned} U_x &= -(af/2 - bc) \\ U_y &= -(af/2 + bc/2), \\ U_z &= (af - bc/2), \\ \eta &= \frac{3bc}{2U}, \end{aligned} \tag{4}$$

where c is a screening correction and estimated as 1.25¹¹⁾. f is the fraction of p character of σ bond and estimated as 0.85¹²⁾. From these equations and with the relation of observed frequency

$$\nu_{obs} = -\frac{eQ_p \cdot U_z}{2} \left(1 + \frac{\eta^2}{3}\right)^{1/2}, \tag{5}$$

all the bond characters are calculated. eQ_p is nuclear quadrupole coupling per p electron. In Cl atom it is 109.6 Mc/sec..

The values of *p*-dichlorobenzene are compared to Dean's values. The difference of η does not affect largely to the bonding characters.

The asymmetry parameter of 8% in *p*-chlorobenzoic acid shows that the hydrogen bond in this molecule is not combined to Cl atom but to oxygen atom of neighbour molecule as indicated from x-ray measurement.

References

- 1) C. Dean and R. V. Pound; J. Chem. Phys. **20** (1952) 195.
- 2) C. Dean; Phys. Rev. **86** (1952) 607.
- 3) B.C. Ituz; Chem. Phys. **22** (1954) 1618.
- 4) H. C. Allen; J. Amer. Chem. Soc. **74** (1952) 6121.
- 5) K. Shimomura; J. Phys. Soc. Japan **12** (1957) 657.
- 6) S. Ogawa; J. Phys. Soc. Japan **12** (1957) 1105.
- 7) R. Bersohn; J. Chem. Phys. **22** (1954) 2078.
- 8) J. Joussoint; Acta. Cryst. **4** (1951) 71.
- 9) H. C. Meal; J. Chem. Phys. **28** (1958) 1180.
- 10) S. Kojima, K. Tsukada and Y. Hinaga; J. Phys. Soc. Japan **10** (1955).
- 11) C. H. Townes and B. P. Daily; J. Chem. Phys. **17** (1949) 782.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, June, 1960

Statistical Mechanics of Antiferromagnetic Layer Crystal, FeCl_2

By SIGEO YOMOSA

Department of Physics, Nara Medical College, Kasihara, Nara

(Received February 23, 1960)

For the spin system in FeCl_2 we developed a statistical theory with Bethe-Peierls method and performed the numerical calculations to compare the results with experimental data of antiferro-ferro transition. Our results are also compared with those obtained by the molecular field approximation. The short range correlation gives rise to the following effects: the decrease of the Néel temperature, more rapid increase of the sublattice magnetization with decreasing temperature, and larger critical magnetic field of antiferro-ferro transition. From the experimental data of the critical magnetic field of antiferro-ferro transition, the values of two exchange coupling constants are estimated. For these values, it is concluded from theoretical considerations that the antiferro-ferro transition is of the first kind in almost whole the temperature region below the Néel point.

§ 1. Introduction

The purpose of this paper is to investigate the statistical properties of the spin systems in FeCl_2 . This substance has a crystalline structure of the CdCl_2 type, in which the metallic ions in the arrangement of close-packed hexagonal layers are imbedded in the close-packed nearly cubic arrangement of the non-metallic ions (the hexagonal axis coinciding with the [111] axis of the cubic arrangement). From neutron diffraction measurements^{1),2),3)} it has been established that the spins of the metallic ions constitute a superstructure of the layer type in ordered state, the hexagonal layers being alternately occupied by up and down spins, i.e., by spins parallel and antiparallel to the $+c$ axis. A theoretical investigation by Kanamori⁴⁾ con-

cluded that the Ising model is well applicable to the spin system of FeCl_2 , the spins being unable to deviate from the c -axis. Although he showed that the statistical properties of this substance are qualitatively well described by the molecular field theory, it is still desirable to take account of the short range correlation between different spins, in order to refine the theory. In this paper we develop such a theory with the Bethe-Peierls approximation.

Starr, Bitter and Kaufmann⁵⁾ and Bizette^{6),7)} found that in FeCl_2 the magnetization shows at low temperatures a sudden increase when the applied field exceeds 10^4 oersted, followed by a gradual increase. This phenomenon has been called "metamagnetism". A theoretical study of this sort of antiferro-ferro transition

under magnetic field was developed by Garrett⁸⁾ and Ziman⁹⁾ and then generalized by Gorter and Van Peski-Tinbergen¹⁰⁾, as well as by Kanamori, Motizuki and Yosida¹¹⁾, all using the molecular field approximation, except Ziman who used the Bethe-Peierls approximation. Garrett has shown that the transition in his specialized model is of the second kind, while Gorter et al. and Kanamori et al. have found that a first kind antiferro-ferro transition occurs in a certain range of temperature when the anisotropy energy is sufficiently large and the ratio of the two exchange constants between spins on similar and dissimilar sites satisfies a certain condition. In ordinary antiferromagnets with small anisotropy energies, an increasing magnetic field causes the spins turn to the direction perpendicular to it before it attains the value required for the antiferro-to-ferro transition. In FeCl_2 , however, the spins are so tightly bound to the hexagonal principal axis that no such turning can occur. The neutron diffraction observation made by Koehler³⁾ showed that the diffraction pattern changes under high magnetic field and he could confirm the sudden antiferro-ferro transition.

Néel¹²⁾ also give an explanation of the metamagnetism of FeCl_2 (as well as that of MnAu_2) by a similar consideration. In Ziman's calculation the exchange interaction within the same sublattice was neglected, which is important in the present case.

According to Kanamori's theory¹⁾, the ground orbital state of Fe^{2+} in the main cubic crystalline field of FeCl_2 is triply degenerate (F_5) and this is further split into a doublet and a singlet by the additional weak trigonal field, the doublet lying lower. In this doublet, the components of the orbital angular momentum have matrices

$$L_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad L_x = L_y = 0.$$

Further the spin-orbit coupling splits this state into five equidistant doublets. Kanamori estimates that the level separation of these doublets is 144°K. Thus, in the vicinity or below the Néel temperature of 24°K, only the lowest doublet ($s_z=2, L_z=1; s_z=-2, L_z=-1$) is populated and therefore the Ising model is applicable. This is further supported by the fact that the entropy change estimated from the specific heat experiment is fairly close to

$R \ln 2$. We shall study this Ising system by the Bethe-Peierls method and calculate the effects of the short range correlation on the Néel temperature, sublattice magnetization, susceptibility and antiferro-ferro transition field.

§2. Quasi-chemical Relations and Free Energy

We consider the system of the hexagonal layers of the iron ions to consist of alternate A and B layers and assume that the Fe^{2+} ions have +spins on layers A and -spins on layers B in ordered state. Namely, we assume a ferromagnetic exchange coupling between neighbouring ions in the same layer and antiferromagnetic super-exchange coupling between neighbouring ions on adjacent layers. We denote the interaction energy by $-A$ for the pair of neighbouring parallel spins in the same layer and by $-A'$ for the neighbouring pair of antiparallel spins on adjacent layers. We consider a system consisting of a central atom on sublattice A or B and its twelve neighbours which couple with the central atom, and number the central atom as 0, the neighbours lying in the same layer as 1, 2, ..., 6, and those lying in the different layers as 7, 8, ..., 12. We denote by $\mu_0 \sigma_i$ the magnetic moment of the i -th atom, and distinguish the spin directions by $\sigma_i = \pm 1$.

When a magnetic field H is applied in the direction parallel to the hexagonal axis, the partition function for the cluster of 1+12 atoms having the central atom on the A -sublattice can be written as

$$\begin{aligned} Z_A = & \sum_{\sigma_0 = \pm 1} \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_7 = \pm 1} \cdots \sum_{\sigma_{12} = \pm 1} \\ & \exp \left[\frac{\mu_0 H}{kT} \sigma_0 + \frac{\mu_0 H_A}{kT} (\sigma_1 + \cdots + \sigma_6) \right. \\ & \quad + \frac{\mu_0 H_B}{kT} (\sigma_7 + \cdots + \sigma_{12}) + \frac{A}{kT} \sigma_0 (\sigma_1 + \cdots + \sigma_6) \\ & \quad \left. - \frac{A'}{kT} \sigma_0 (\sigma_7 + \cdots + \sigma_{12}) \right], \quad (1) \end{aligned}$$

where H_A is the effective field acting on atoms 1, 2, ..., 6 of the A -sublattice and H_B that acting on atoms 7, 8, ..., 12 of the B -sublattice. These H_A and H_B can be determined as functions of the field H and temperature T from conditions that the mean values of the magnetic moments of the atoms in equivalent positions are equal. Now, writing briefly as

$\mu_0 H/kT = I$, $\mu_0 H_A/kT = I'$, $\mu_0 H_B/kT = I''$, $A/kT = J$, $A'/kT = J'$, we have

$$\begin{aligned} Z_A &= \sum_{\sigma_0=\pm 1} e^{\sigma_0 I} \prod_{j=1}^6 \left(\sum_{\sigma_j=\pm 1} e^{(I'+J\sigma_0)\sigma_j} \right) \times \\ &\quad \times \prod_{j=1}^6 \left(\sum_{\sigma_j=\pm 1} e^{(I''-J'\sigma_0)\sigma_j} \right) \\ &= e^I [2\text{ch}(I'+J)]^6 [2\text{ch}(I''-J')]^6 \\ &\quad + e^{-I} [2\text{ch}(I'-J)]^6 [2\text{ch}(I''+J')]^6 = Z_A^+ + Z_A^-, \end{aligned} \quad (2)$$

where Z_A^+ and Z_B^- represent the relative probabilities for $\sigma_0 = +1$ and -1 , respectively. So we have

$$\langle \sigma_0 \rangle_{av} = \frac{Z_A^+ - Z_A^-}{Z_A}.$$

On the other hand, we have for any one of the atoms $j=1, 2, \dots, 6$

$$\begin{aligned} \langle \sigma_j \rangle_{av} &= \frac{1}{6} \left\langle \sum_{i=1}^6 \sigma_i \right\rangle_{av} = \frac{1}{6} \frac{\partial}{\partial I'} \log Z_A \\ &= \frac{1}{Z_A} [Z_A^+ \text{th}(I'+J) + Z_A^- \text{th}(I'-J)]. \end{aligned}$$

So the condition $\langle \sigma_0 \rangle = \langle \sigma_j \rangle$ can be expressed as

$$\left[\frac{\text{ch}(I'+J)}{\text{ch}(I'-J)} \right]^6 \left[\frac{\text{ch}(I''-J')}{\text{ch}(I''+J')} \right]^6 = e^{2(I'-I)}. \quad (3)$$

A similar relation is obtained from the partition function for the cluster having the central atom on the B -sublattice, that is,

$$\left[\frac{\text{ch}(I''+J)}{\text{ch}(I''-J)} \right]^6 \left[\frac{\text{ch}(I'-J')}{\text{ch}(I'+J')} \right]^6 = e^{2(I''-I)}. \quad (4)$$

In the case of vanishing external field, $H=0(I=0)$, it can be shown that a solution $I'=I''=0$ exists at any temperature and another solution $I'=-I''$ below a certain temperature (the Néel temperature). If we put $I'=-I''$ in equation (3), take its logarithm and expand it in powers of I' , assuming I' to be small, we have

$$\begin{aligned} 2I' &= 10\text{th}J \left[I' - \frac{I'^3}{3} \text{ch}^{-2}J + \dots \right] \\ &\quad + 12\text{th}J' \left[I' - \frac{I'^3}{3} \text{ch}^{-2}J + \dots \right] \end{aligned}$$

Then, we can find a finite value of $I'=-I''$: $I'^2 = I''^2$

$$= \frac{3\text{ch}^3 J \text{ch}^3 J'}{5\text{ch}^3 J' \text{sh}J + 6\text{ch}^3 J \text{sh}J'} [5\text{th}J + 6\text{th}J' - 1 + \dots]$$

and can determine the Néel temperature T_N from

$$1 = 5\text{th}J + 6\text{th}J'. \quad (5)$$

Now, we rewrite equation (1) as follows:

$$Z_A = \sum_{\sigma_0=\pm 1} \sum_{\sigma_1=\pm 1} e^{I\sigma_0 + I'\sigma_1 + J\sigma_0\sigma_1} [2\text{ch}(I'+I\sigma_0)]^6 [2\text{ch}(I''-I'\sigma_0)]^6 \quad (6)$$

$$= \sum_{\sigma_0=\pm 1} \sum_{\sigma_7=\pm 1} e^{I\sigma_0 + I'\sigma_7 - J'\sigma_0\sigma_7} [2\text{ch}(I'+J\sigma_0)]^6 [2\text{ch}(I''-J'\sigma_0)]^6. \quad (6')$$

Each summand of the right-hand side of (6) gives the relative probability of an assigned combination of $\sigma_0=\pm 1$ and $\sigma_1=\pm 1$. So, if $\langle Q_{A++} \rangle$, $\langle Q_{A--} \rangle$ and $\langle Q_{A+-} \rangle$ are the mean numbers of $++$, $--$ and $+-$ pairs of nearest neighbours on A -sublattice, we have the following quasi-chemical relations for the pairs within the same layer:

$$\frac{\langle Q_{A+-} \rangle^2}{\langle Q_{A++} \rangle \langle Q_{A--} \rangle} = 4e^{-4J} = \frac{\langle Q_{B+-} \rangle^2}{\langle Q_{B++} \rangle \langle Q_{B--} \rangle}. \quad (7)$$

Similarly, from the right-hand side of (6)' we have the following quasi-chemical relation for the pairs between layers:

$$\frac{\langle R_{++} \rangle \langle R_{--} \rangle}{\langle R_{+-} \rangle \langle R_{-+} \rangle} = e^{-4J'}, \quad (8)$$

where R_{+-} , etc. are the numbers of pairs which have $+$ spin on A -sublattice and $-$ spin on B -sublattice. Furthermore, denoting by N_{A+} , N_{A-} , N_{B+} and N_{B-} the numbers of $+$

and $-$ spins on A and B sublattices, respectively, we have the following relations:

$$2Q_{A++} + Q_{A+-} = 6N_{A+}, \quad 2Q_{A--} + Q_{A+-} = 6N_{A-}, \quad (9)$$

$$2Q_{B++} + Q_{B+-} = 6N_{B+}, \quad 2Q_{B--} + Q_{B+-} = 6N_{B-}, \quad (10)$$

$$R_{++} + R_{+-} = 6N_{A+}, \quad R_{--} + R_{-+} = 6N_{A-}, \quad (11)$$

$$R_{++} + R_{-+} = 6N_{B+}, \quad R_{--} + R_{+-} = 6N_{B-}, \quad (12)$$

$$N_{A+} + N_{A-} = N_A = N/2, \quad N_{B+} + N_{B-} = N_B = N/2, \quad (13)$$

where N is the total number of the lattice sites. Of the four equations of (11) and (12), three are independent. Therefore we have nine independent relations for fourteen parameters (N_{A+} , N_{A-} , N_{B+} , N_{B-} , Q_{A++} , Q_{A+-} , Q_{A--} , Q_{B++} , Q_{B+-} , Q_{B--} , R_{++} , R_{+-} , R_{-+} , R_{--}), and so we have to regard five parameters as independent.

The energy of the system can be written

as a function of five parameters as

$$\begin{aligned} W(N_{A+}, N_{B+}, Q_{A+-}, Q_{B+-}, R_{+-}; H, T) \\ = -A(Q_{A++} + Q_{A--} - Q_{A+-} + Q_{B++} + Q_{B--} - Q_{B+-}) \\ + A'(R_{++} + R_{--} - R_{+-} - R_{-+}) \\ - \mu_0(N_{A+}N_{B+} - N_{A-}N_{B-}) \\ = -3N(A - A') + 2A(Q_{A+-} + Q_{B+-}) \\ - 2A'[2R_{+-} - 6(N_{A+} - N_{B+})] \\ - \mu_0 H[2(N_{A+} + N_{B+}) - N]. \end{aligned} \quad (14)$$

For given N_{A+} and N_{B+} , the average value of the energy is related to the free energy F by

$$\begin{aligned} \langle W(N_{A+}, N_{B+}, \langle Q_{A+-} \rangle, \langle Q_{B+-} \rangle, \langle R_{+-} \rangle; H, T) \rangle \\ = \partial[F(N_{A+}, N_{B+}; H, T)/T] / \partial \left[\frac{1}{T} \right]. \end{aligned} \quad (15)$$

Integrating this equation, we obtain

$$F/T = (F/T)_\infty - \int_\infty^T \frac{\langle W \rangle}{T^2} dT, \quad (16)$$

where $(F/T)_\infty$ can be expressed by the total number of spin configurations for fixed N_{A+} and N_{B+} , as

$$(F/T)_\infty = \left(\frac{\langle W \rangle}{T} \right)_{T=\infty} - (S)_{T=\infty}$$

$$\begin{aligned} = -k \log \left[\frac{N/2!}{N_{A+}! \left(\frac{N}{2} - N_{A+} \right)!} \right. \\ \left. \times \frac{N/2!}{N_{B+}! \left(\frac{N}{2} - N_{B+} \right)!} \right]. \end{aligned} \quad (17)$$

Now, introducing order parameters $s (1 \geq s \geq 0)$ and $s' (1 \geq s' \geq -1)$ by $N_{A+} = N(1+s)/4$, $N_{B+} = N(1+s')/4$, and by making use of equation (7), (9) and (13), we have

$$\langle Q_{A+-} \rangle = \frac{3N}{2} \frac{[1 + (1-s^2)(e^{4A/kT} - 1)]^{\frac{1}{2}} - 1}{e^{4A/kT} - 1}. \quad (18)$$

Similarly, from (7), (10) and (13),

$$\langle Q_{B+-} \rangle = \frac{3N}{2} \frac{[1 + (1-s'^2)(e^{4A'/kT} - 1)]^{\frac{1}{2}} - 1}{e^{4A'/kT} - 1}. \quad (19)$$

and from (8), (11), (12) and (13)

$$\begin{aligned} \langle R_{+-} \rangle = \frac{3N}{4} \left[(2+s-s') + \frac{2}{e^{4A'/kT} - 1} \right] \\ - \frac{3N}{4} \left[\left(2+s-s' + \frac{2}{e^{4A'/kT} - 1} \right)^2 \right. \\ \left. - \frac{4e^{4A'/kT}}{e^{4A'/kT} - 1} (1+s)(1-s') \right]^{\frac{1}{2}}. \end{aligned} \quad (20)$$

Furthermore, from (16) and (17), the following free energy expression is obtained after a somewhat complicated calculation:

$$\begin{aligned} F(s, s'; H, T) = \frac{NkT}{4} \left[-12(A/kT - A'/kT) - 2\frac{\mu_0 H}{kT}(s+s') \right. \\ + \{ (1+s) \log(1+s) + (1-s) \log(1-s) + (1+s') \log(1+s') + (1-s') \log(1-s') - 4 \log 2 \} \\ + 3 \left\{ (1+s) \log \frac{\alpha+s}{1+s} + (1-s) \log \frac{\alpha-s}{1-s} - 2 \log \frac{\alpha+1}{2} \right. \\ \left. + (1+s') \log \frac{\alpha'+s'}{1+s'} + (1-s') \log \frac{\alpha'-s'}{1-s'} - 2 \log \frac{\alpha'+1}{2} \right\} \\ - 6 \left\{ \log \frac{\sqrt{1-\frac{1-ss'}{2}}\gamma + 1}{2(1-\gamma)} - \frac{s-s'}{2} \log \frac{\sqrt{1-\frac{s-s'}{2}}\gamma + \frac{1-ss'}{s-s'}}{1 + \frac{1-ss'}{s-s'}} \right. \\ \left. - \frac{s+s'}{2} \log \frac{\sqrt{1-\frac{s+s'}{2}}\gamma + \frac{1+ss'}{s+s'}}{\left(1 + \frac{1+ss'}{1+s'} \right)(1-\gamma)} \right\} \Bigg], \end{aligned} \quad (21)$$

where

$$\begin{aligned} \alpha^2 &= 1 + (1-s^2)(e^{4A/kT} - 1), \\ \alpha'^2 &= 1 + (1-s'^2)(e^{4A'/kT} - 1). \end{aligned}$$

$$\Gamma(\gamma) = \frac{(s-s')^2}{4} \gamma^2 - (1-ss')\gamma + 1, \quad \gamma = 1 - e^{-4A'/kT}.$$

(22)

For the sake of comparison, the free energy in the Bragg-Williams or molecular field approximation will also be given here. This is obtained by putting $J = J' = 0$ in the right-hand side terms of the quasi-chemical relations. Or it can be obtained readily using the probabilities of finding + or - spin on each

lattice site. That is,

$$F^m = -\frac{3}{2}NA(s^2 + s'^2) + 3NA'ss' - \frac{N}{2}\mu_0 H(s + s') \\ + \frac{NkT}{4}[(1+s)\log(1+s) + (1-s)\log(1-s) \\ + (1+s')\log(1+s') + (1-s')\log(1-s') \\ - 4\log 2] \quad (23)$$

From the minimum condition of this free energy with respect to the parameters s and s' , or the sublattice magnetization $M_A = N\mu_0 s/2$, $M_B = N\mu_0 s'/2$, the total magnetization $M_A = N\mu_0(s + s')/2$ can be determined as functions of H and T .

We shall calculate in the following sections the critical data and the magnetic and caloric quantities of our spin system, using the free energy expressions (21) and (23).

§ 3. The Néel Temperature

It is expected that in FeCl_2 there is a strong

ferromagnetic coupling in the same layer and a weak antiferromagnetic coupling between adjacent layers. To simplify our numerical calculation, we shall rather arbitrarily put $A = 10A'$; it will be shown later (§ 8) that this ratio is reasonable. For this ratio of the coupling constants the Néel temperature is calculated to be $T_N = A/(0.180k)$ from (5) (k : Boltzmann constant). Since the observed T_N is 24°K , we have $A = 10A' = 0.18 \times 24k = 4.32k$. The parameter γ defined by (22) is therefore small compared with 1 over a wide range of temperature, i.e., above a few degree absolute. At $T = T_N$, $\gamma = 0.069$. Thus for such temperatures, we may expand the free energy expression in powers of γ and take terms up to order γ^2 . In fact, the free energy value at the Néel temperatures calculated up to first order of γ is in error only by one percent. The free energy expression including terms of order γ^2 is

$$F(s, s'; H, T) = -3N(A - A') - \frac{N}{2}\mu_0 H(s + s') \\ - \frac{N}{2}kT \left\{ (1+s)\log(1+s) + (1-s)\log(1-s) \right. \\ \left. + (1+s')\log(1+s') + (1-s')\log(1-s') - 4\log 2 \right\} \\ - \frac{3}{4}NkT \left\{ 1 - ss' - \gamma^2 \left[4(1+ss' - 1-s^2)(1-s'^2) \right] + \dots \right\} + \frac{3}{2}NkT \log(1-\gamma) \\ - \frac{3}{4}NkT \left\{ \frac{1+s}{1-s} \log \frac{\alpha+s}{\alpha-s} + \frac{1-s}{1-s'} \log \frac{\alpha-s}{\alpha-s'} - 2\log(\alpha+1) \right. \\ \left. + \frac{1+s'}{1-s'} \log \frac{\alpha'+s'}{\alpha'-s'} + \frac{1-s'}{1-s'} \log \frac{\alpha'-s'}{\alpha'-s'} - 2\log(\alpha'+1) \right\} \quad (24)$$

From the conditions $\partial F/\partial s = 0$, $\partial F/\partial s' = 0$, we obtain

$$\left. \begin{aligned} -\frac{\mu_0 H}{kT} - \log \frac{1+s}{1-s} + \frac{3}{2} \log \frac{\alpha+s}{\alpha-s} + \frac{3}{8} \gamma^2 s + \frac{3}{4} \gamma(\gamma+2)s' - \frac{3}{8} \gamma^2 ss'^2 &= 0, \\ -\frac{\mu_0 H}{kT} - \log \frac{1+s'}{1-s'} + \frac{3}{2} \log \frac{\alpha'+s'}{\alpha'-s'} + \frac{3}{8} \gamma^2 s' + \frac{3}{4} \gamma(\gamma+2)s - \frac{3}{8} \gamma^2 s^2 s' &= 0. \end{aligned} \right\} \quad (25)$$

The Néel temperature is determined by the following conditions:

$$\left. \begin{aligned} \left(\frac{\partial^2 F}{\partial s \partial s'} \right)^2 - \left(\frac{\partial^2 F}{\partial s^2} \right) \left(\frac{\partial^2 F}{\partial s'^2} \right) &= 0, \\ \partial^2 F / \partial s^2 > 0, \quad \partial F / \partial s = \partial F / \partial s' = 0, \quad s = s' = 0. \end{aligned} \right\} \quad (26)$$

Putting $A = 10A'$ and $H = 0$ (vanishing external field), we can obtain the ratio of the Néel temperature to A to order γ from

$$2 - 3\gamma^2 A^2 / T_N^2 + \frac{3}{2} \gamma^2 T_N^2 = 0, \\ T_N = A/(0.178k). \quad (27)$$

Thus the value of T_N calculated from this equation agrees practically with that calculated from (5).

With the molecular field approximation, one would obtain $T_N = A/(0.153k)$.

§ 4. Sublattice Magnetization

In vanishing external field, $H = 0$, the order parameters s and s' are determined as functions of temperature by the following equation which is obtained from (25) by putting $s = s^0$, $s' = -s^0$:

$$\begin{aligned}
 &-\log \frac{1+s_0}{1-s_0} + \frac{3}{2} \log \frac{\alpha_0+s_0}{\alpha_0-s_0} \\
 &-\left\{ \frac{3}{8} r^2 (1+s_0^2) + \frac{3}{2} r \right\} s_0 = 0, \qquad (28) \\
 &\alpha_0 = \alpha(s_0).
 \end{aligned}$$

The corresponding equation in the molecular field approximation follows from equation (23) as:

$$\log \frac{1+s_0^m}{1-s_0^m} = \frac{12}{kT} (A+A') s_0^m, \qquad (29)$$

where s_0^m indicates the value of s for $H=0$ in the molecular field approximation. Fig. (1) shows the variation of the order parameter s_0 (or the sublattice magnetization $M_A=M_B=N\mu_0 s_0/2$) and that of s_0^m as functions of temperature. It is seen that the establishment of order with decreasing temperature is more rapid with the Bethe-Peierls approximation than the molecular field approximation.

§ 5. Parallel Susceptibility

In the presence of a small external field H parallel to the hexagonal axis, the parameters s, s' take values $s=s_0+\epsilon, s'=-s_0+\epsilon$. The small quantity ϵ is determined as a function of H and T from (25) and (28), and we find the parallel susceptilits $\chi_{||}$ for $T \leq T_N$:

$$\begin{aligned}
 \chi_{||} &= M/H = N\mu_0 \epsilon/H \\
 &= \frac{C}{T} \left[\frac{1}{1-s_0^2} \left(\frac{3}{\alpha_0} - 2 \right) + \left(\frac{3}{2} + \frac{9}{8} r + \frac{3}{8} r s_0^2 \right) r \right]^{-1}, \qquad (30)
 \end{aligned}$$

where $C=N\mu_0^2/k$. The paramagnetic susceptibility for $T \geq T_N, \chi_p$, is obtained as

$$\chi_p = \frac{C}{T} \left[\frac{3}{\alpha_0} - 2 + \left(\frac{3}{2} + \frac{9}{8} r \right) r \right]^{-1}. \qquad (31)$$

The curve of $1/\chi_p$ vs T is not a straight line as it is in the molecular field approximation. However, at high temperatures, we have

$$\chi_p = \frac{C}{T-6(A-A')/k} \equiv \frac{C}{T-0.97T_N}. \qquad (32)$$

The corresponding formulae in the molecular field theory are

$$\begin{aligned}
 \chi_{||}^m &= \frac{C}{T/(1-s_0^2)-6(A-A')/k} \\
 &\equiv \frac{C}{T/(1-s_0^2)-0.82T_N^m} (T \leq T_N^m), \\
 \chi_p^m &= \frac{C}{T-6(A-A')/k} \equiv \frac{C}{T-0.82T_N^m} (T \geq T_N^m). \qquad (33)
 \end{aligned}$$

The value of the susceptibility at the Néel point in the Bethe-Peierls approximation is slightly larger than that in the molecular field approximation:

$$\chi_N = 0.89 \frac{\mu_0 M_0}{A} > \chi_N^m = 0.83 \frac{\mu_0 M_0}{A}; \quad \chi_N/\chi_N^m = 1.07.$$

The calculated susceptibility curves are shown also in Fig. (1) in reduced scale.

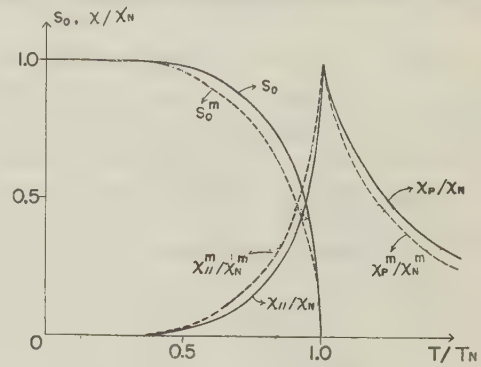


Fig. 1. Order parameter and susceptibility vs. temperature in reduced scale. The solid curves represent the present results and the dashed curves are obtained from the molecular field approximation.

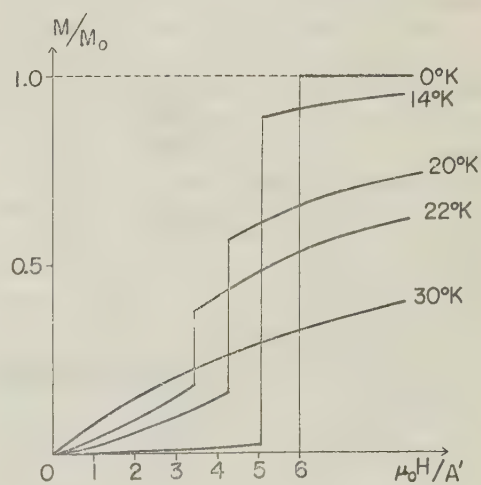


Fig. 2. Magnetization curves representing the antiferro-ferro transition which obtained from our calculation.

§ 6. Antiferro-ferro Transition by the Application of a Magnetic Field

When we solve s and s' from (25), two possible solutions can be found: antiferromagnetic solution and paramagnetic (or, rather ferromagnetic) solution. Magnetization vs. field curves corresponding to these solutions

are drawn in Fig. (2) for various values of temperature. The transition field from the antiferromagnetic state to the paramagnetic state can be determined by the law of equal area, as shown in Fig. (3) (area $B_1B_2B_3$ =area $B_3B_4B_5$) where we compare the magnetization curve at 20°K in the Bethe-Peierls approximation with that in the molecular field approximation. The critical field (transition field)

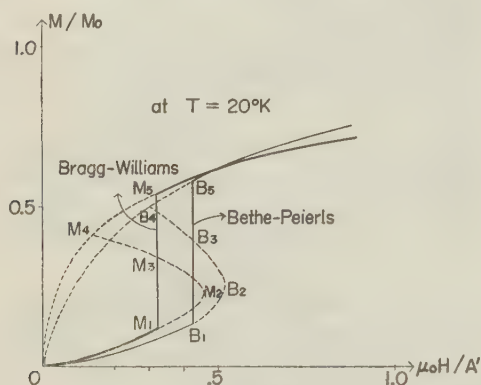


Fig. 3. Comparison between the transition curves obtained by the Bethe-Peierls approximation and that obtained by the molecular field approximation.

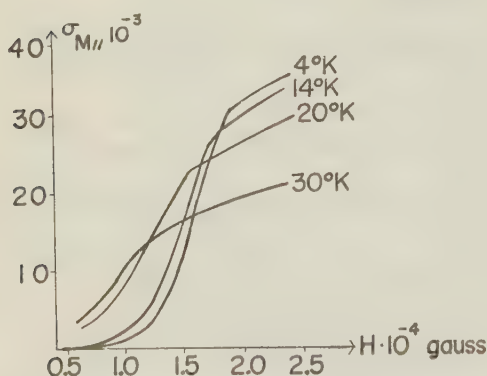


Fig. 4. Magnetization curves measured by Bizette et al.⁷⁾

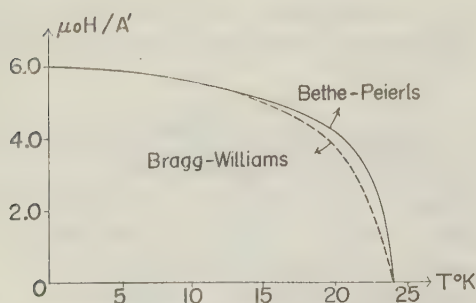


Fig. 5. Transition field vs. temperature.

vs. temperature is plotted in Fig. (5). The corresponding experimental results due to Bizette et al.⁷⁾ are shown in Fig. (4). Although we find only a qualitative agreement, the experimental results are open to arguments in that the magnetization did not reach saturation even at a field as strong as 25000 oer and that the magnetization curve at 30°K (above the Néel temperature) showed a trace of the antiferro-ferro transition.

Kanamori, Motizuki and Yosida¹¹⁾ previously discussed this transition by the molecular field approximation and found that the transition is no longer of the first kind beyond the temperature T^* given by

$$T^*/T_N = (3A - A')/3A;$$

it becomes of the second kind for $T^* < T < T_N$, if $1 \geq A/(A + A') \geq 3/8$. In our case ($A = 10A'$), this last condition is satisfied and we have $T^*/T_N = 0.967$. The existence of such a temperature also in our approximation can be seen in the following way. First we note that the field strength at which the antiferromagnetic state joins the paramagnetic state (point B_4 in Fig. 3) is characterized by the vanishing of the parameter $q = (s - s')/2$. Then we see that T^* is the temperature at which the magnetization curve has an infinite slope for $q \rightarrow 0$, or $\lim_{q \rightarrow 0} dp/dH = \infty$, where $p = (s + s')/2$. Above T^* , $\lim_{q \rightarrow 0} dp/dH$ should be positive if the transition is to be of the second kind. Now, to estimate T^* , we assume that s and s' have small values, since we expect T^* to be close to T_N , and expand the logarithmic terms of equations (25) in power of s and s' . Further, we neglect terms of order γ^2 . Then the two equations of (25) become as follows;

$$a(p+q) + b(p-q) - c(p+q)^3 - h + \dots = 0, \quad (34)$$

$$a(p-q) + b(p+q) - c(p-q)^3 - h + \dots = 0, \quad (35)$$

where $a = 2e^{-2A/kT} - 2$, $b = 3\gamma/2 = 3(1 - e^{-A'/kT})/2$, $c = 2/3 - 3e^{-A/kT}/2 + 1e^{-6A/kT}/2$, $h = \mu_0 H/kT$. From these equations, we obtain p^2 in powers of q :

$$p^2 = (a-b)/3c - \frac{1}{3}q^2 + \dots \quad (36)$$

With a fixed temperature, we differentiate (34) with respect to H and calculate the value of $\lim_{q \rightarrow 0} dp/dH$. In this calculation we need the value of d^2p/dq^2 (as $dp/dq \rightarrow 0$ for $q \rightarrow 0$), which can be obtained from (36). The result is

$$\lim_{q \rightarrow 0} dp/dH = -\frac{\mu_0/kT}{2(2b-3a)} \\ = \frac{\mu_0/kT}{6(3e^{-2A/kT} + e^{-4A'/kT} - 3)} \quad (37)$$

This quantity becomes infinite when $T/T_N = T^*/T_N = 0.975$, positive above this temperature and negative below it. This ratio of the temperature T^* to T_N in Bethe-Peierls approximation is slightly higher than that in the molecular field approximation. However, as this temperature is very close T_N (0.6° below $T_N = 24^\circ\text{K}$), it will have no practical importance.

§ 7. Jump in Specific Heat and Change in Entropy

Formulae for the entropy and specific heat can be calculated by the usual procedure. We shall give only the results for the jump of the specific heat at the Néel temperature and the entropy value at this temperature. The former is $\Delta C_V = C_{T_N-0} - C_{T_N+0} = 2.43 - 0.16 = 2.27$ cal deg $^{-1}$ mol $^{-1}$, in contrast to a jump of 1.99 cal deg $^{-1}$ mol $^{-1}$ with the molecular field approximation, and the latter is $(\Delta S)_0^T = 0.64Nk = 1.27$ cal deg $^{-1}$ mol $^{-1}$, while obviously the total entropy change should be $(\Delta S)_0^\infty = k \log 2^N = 0.69Nk = 1.37$ cal deg $^{-1}$ mol $^{-1}$; thus only 1/14 of the total entropy remains beyond the Néel temperature. The experimental entropy change is estimated from the measured specific heat curve¹³⁾ to be about 1.4 cal deg $^{-1}$ mol $^{-1}$, of which about 10% are distributed above the Néel temperature.

§ 8. Evaluation of A and A'

The two parameters, A and A' , contained in our theory and their ratio A/A' can be evaluated in the following way. The antiferro-ferro transition field H at absolute zero is related to A' by the relation $\mu_0 H = 6A'$ (see Fig. 2). This field at absolute zero has been observed⁷⁾ to be about 1.1×10^4 oe. In order to correct this field for the demagnetizing field, we must know the magnitude of the sublattice magnetizations. Assuming $\langle L \rangle = 1$ and $g_s = 2.0$, the magnetic moment of an Fe^{2+} ion will be $\mu_0 = (2g_s + \langle L \rangle)\mu_B = 5\mu_B$ and the sublattice magnetization $M = \mu_0 N/2 = 357$ gauss par c.c.. Therefore the demagnetizing field will be of the order of $(4\pi M/3) \times 2 = 3000$ oe.

The value of the transition field at absolute zero corrected for this demagnetizing field will thus be about 8000 oe. The relation $\mu_0 H/A' = 6$ then gives $A' = 0.447k$. With this value, and the observed value of $T_N (= 24^\circ\text{K})$, we obtain from (5) (where $J = A/kT_N$ and $J' = A'/kT_N$) $A = 4.31k$, and so $A = 9.7A'$. The ratio $A/A' = 10$ used in our preceding calculations is therefore seen to be reasonable.

§ 9. Discussion and Summary

We performed the numerical calculations for the spin system of FeCl_2 with the Bethe-Peierls method and the molecular field approximation and compared the results obtained by these two methods. The short range correlation gives rise to the following four effects: (1) the decrease of the Néel temperature, as given by the ratio $T_N/T_N^m = 0.153/0.180 = 0.85$, where T_N^m is the Néel temperature by the molecular field approximation, (2) more rapid increase of the sublattice magnetization with decreasing temperature, (3) steeper decrease of the parallel susceptibility with decreasing temperature, below the Néel temperature, and more lenient decrease of the paramagnetic susceptibility above the Néel temperature, and (4) larger critical magnetic field of antiferro-ferro transition. From the experimental data of the critical field of antiferro-ferro transition and the Néel temperature, the value of the two exchange coupling constants and their ratio can be estimated as about $A \approx 4.3k$, $A' \approx 0.45k$ and $A/A' \approx 9.7$. For such values of A and A' , it is concluded from theoretical considerations that the antiferro-ferro transition is of the first kind in almost whole the temperature region below the Néel point. In order to estimate more correct values of the exchange constants A , A' and to make clear the doubtful points which we have pointed out in § 6, it is desirable to make more refined experiment on the antiferro-ferro transition under magnetic field. On the other hand, since the numerical calculation is laborious even in the Bethe-Peierls approximation, it seems unpractical to elevate the order of approximation.

The author is indebted to Prof. T. Nagamiya and the members of his laboratory for helpful discussions, and especially he wishes to thank Mr. H. Suzuki for the help in numerical calculations.

Reference

- 1) M. K. Wilkinson and J. W. Cable: Bull. Amer. Phys. Soc. **1** (1856) No. 4, 190.
- 2) A. Herpin and P. Mériel: Compt. rend. **245** (1957) 650.
- 3) W. C. Koehler, M. K. Wilkinson, J. W. Cable and E. O. Wollan: J. phys. radium **20** (1959) 180. M. K. Wilkinson, J. W. Cable, E. O. Wollan and W. C. Koehler: Phys. Rev. **113** (1959) 497.
- 4) J. Kanamori: Progr. Theor. Phys. **20** (1958) 890.
- 5) C. Starr, F. Bitter and A. R. Kaufmann: Phys. Rev. **58** (1940) 997.
- 6) H. Bizette: Ann. physique (12) **1** (1946) 316; Thesis (1946) 84; J. phys. radium **12** (1951) 161.
- 7) H. Bizette, C. Terrier and B. Tsai: Compt. rend. **243** (1956) 895, 1295.
- 8) C. G. B. Garrett: J. Chem. Phys. **19** (1951) 1154.
- 9) J.M. Ziman: Proc. Phys. Soc. London **64** (1951) 1108.
- 10) C. J. Gorter and T. van Peski-Tinbergen: Physica **22** (1956) 273.
- 11) J. Kanamori, K. Motizuki and K. Yosida: Busseiron Kenkyu **63** (1953) 28 (in Japanese). For the essentials of this paper, refer J. Kanamori: *Magnetic Properties of the Iron-Group Anhydrous Chlorides*, Progr. Theor. Phys. **20** (1958) 890 and K. Motizuki: *Metamagnetism of Methylamine Chrome Alum*, J. Phys. Soc. Japan **14** (1959) 759.
- 11) L. Néel: Compt. rend. **242** (1956) 1949.
- 13) O. Trapeznikowa and L. Schubnikow: Phys. Z. Sowjetunion **7** (1935) 66.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Ionization in Argon Mixtures by Electrons in an Electric Field

by Mikiya Yamane

*Hitachi Central Research Laboratory
Kokubunji-machi, Tokyo*

(Received January 23, 1960)

A systematic investigation has been made on ionization in argon mixtures by electrons in a convergent field. Total filling pressure is 760 mmHg and the added impurities are organic vapors and inert gases.

The ionization current increases by the addition of these impurities even when their ionization potentials are higher than the metastable potential of argon.

The increase in ionization seems to become more remarkable as the ionization potential of the impurity lowers and the optimum concentration that gives a maximum ionization decreases with the effectiveness of the added impurities.

From the result of a series of our measurement possibility of direct impact ionization and photoelectric ionization is suggested.

§1. Introduction

Although the very interesting feature of an increase in ionization in neon-argon mixtures has been well known since the detailed studies of A. A. Kruithoff and F. M. Penning in 1936-1940¹⁾, knowledge of ionization in other different mixtures of gases is still in a very unsatisfactory state. It has been generally agreed that in Ne-A

mixtures the increase in ionization is due to the metastable neon atoms, which transfer their excitation energy and ionize argon atoms. The influence of the admixture on the ionization rate is so high that it has been believed that just the "Penning effect" could be competent for a convincing quantitative explanation.

Furthermore, several other experiments

have been generally consistent with this basic assumption of energy transfer from metastable atoms to impurities. Penning²⁾ investigated the sparking potential of neon with a small admixture of argon irradiating with visible Ne light and observed an increase in the sparking potential. Recently T. Nakaya³⁾ carried out similar experiments for A-Hg mixtures under illumination of a Hg arc lamp or an incandescent lamp and obtained the same effect.

These experiments favor Penning effect in that the metastable atoms will perform a predominant role in the ionization of mixture gases.

However, it is worthy of our notice that the average energy loss per ion pair produced by α -particles decreases in mixture gases, as C. E. Melton et al⁴⁾ have recently demonstrated clearly. Their experiment indicated that even a small amount of a foreign gas, whose ionization potential is higher than the metastable potential of the main gas, lowers the value of the energy loss per ion pair.

The result of C. E. Melton et al. suggests a similar increase of ionization in mixture gases in the case of electron collision in an electric field. However, if a foreign gas, whose ionization potential is higher than the metastable potential of the main gas, would give rise to an increase in ionization, it should be a matter of prime concern in gaseous discharge in mixture gases. It is for this reason that the present work is undertaken.

In the present work an attempt has been made to make a systematic experiment and to form a consistent picture of the multiplication process in mixture gases. The ionization current is measured in argon with admixture of organic vapors and inert gases at a total filling pressure of 760 mm Hg. To obtain informations of the effect of different admixtures and to provide a basis of comparison between them the same procedure is adopted throughout the experiments.

§ 2. Experimental Procedure

The experimental tube used in this investigation is shown in Fig. 1. The electrodes are two concentric cylinders of very different radii. Anode is a tungsten central wire of 0.2 mm in diameter, the ends of which are

shielded by a glass bead and a glass guard tube to avoid regions of abnormally high electric field, and cathode is a copper outer cylinder of 30 mm in diameter and 70 mm in length.

To investigate the initial build up of the gas multiplication RaD of about $4\mu\text{C}$ is mounted in the tube such that α -particles from RaF enter the active region in direction of the axis and expend all of their energy in the gas.

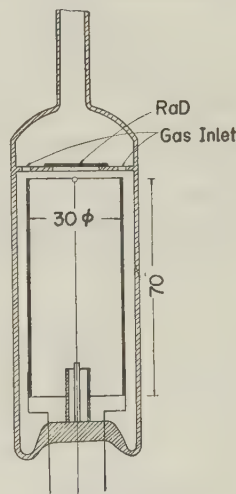


Fig. 1. Experimental tube for measuring ionization current.

Before filling gas mixtures, the entire gas filling system is evacuated down to 10^{-6} mm Hg, but the tube is not baked for fear of the evaporation of the radio-active substance.

Throughout the experiments filling pressure of argon and argon mixture gases is 760 mm Hg in order to facilitate analysis of the ionization in mixture gases. The purity of the gases used is above 99.9%.

The ionization current measured with a vibrating reed electrometer is plotted against applied voltage from the range of the saturation current (ionization chamber) to that of the gas multiplication (proportional counter).

§ 3. Results

3.1 Argon-Alkanes

The ionization current plotted against voltage for argon-alkanes mixtures at a total pressure of 760 mmHg is shown in figures from Fig. 2 to Fig. 6. Alkanes used in our measurements are methane, ethane, propane,

normal-butane, iso-butane, normal-pentane, and iso-pentane. The concentration of alkanes in mixture gases is indicated by the figures on the curves.

In pure argon the region of the saturation

current, i_0 , extends from 50V to about 350V, yielding a saturation current of about 1.75×10^{-10} A. Beyond 350V is seen an approximately exponential rise of current and the ratio of the ionization current to the saturation current i/i_0 is given by the equation

$$\frac{i}{i_0} = \exp \int_{x_0}^a \alpha dx \quad (1)$$

where a is the radius of the central wire, x_0 the distance from the center of the wire at which avalanche starts and α is the Townsend ionization coefficient.

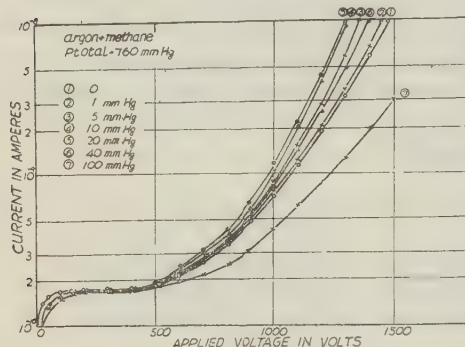


Fig. 2. Ionization current in argon-methane mixtures at $P_{total}=760$ mm. Partial pressure of methane is indicated by the figures on the curves.

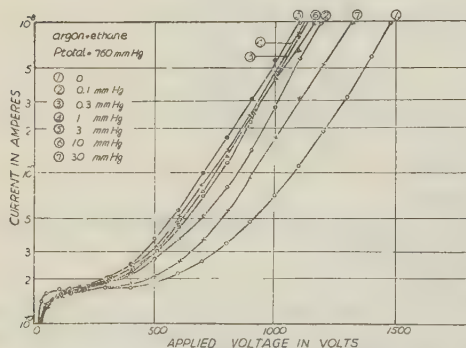


Fig. 3. Ionization current in argon-ethane mixtures at $P_{total}=760$ mm Hg. Partial pressure of ethane is indicated by the figures on the curves.

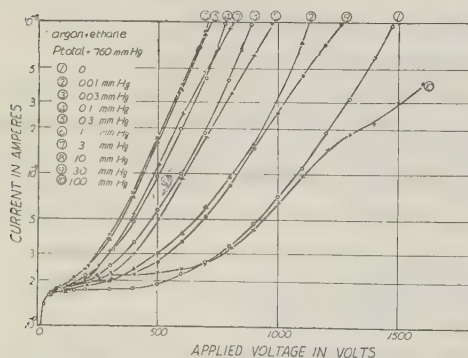


Fig. 4. Ionization current in argon-propane mixtures at $P_{total}=760$ mm Hg. Partial pressure of propane is indicated by the figures on the curves.

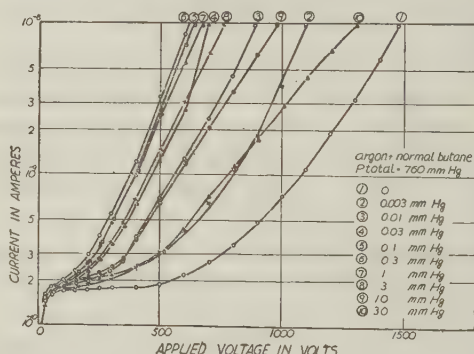


Fig. 5. Ionization current in argon-butane mixtures at $P_{total}=760$ mm Hg. Partial pressure of butane is indicated by the figures on the curves.

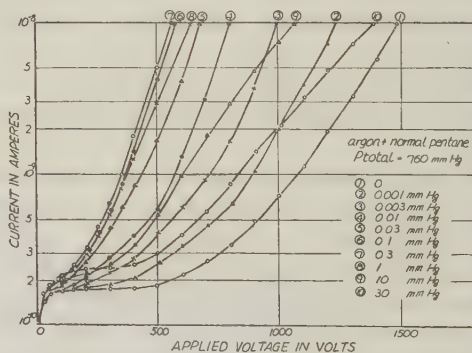


Fig. 6. Ionization current in argon-pentane mixtures at $P_{total}=760$ mm Hg. Partial pressure of pentane is indicated by the figures on the curves.

To provide a basis for the reliability of the values of α/P obtained from the ionization curves in convergent field, our values of α/P and Kruithoffs data are compared in Table I. A method of calculating α/P in a convergent field will be described in Sec. 4.

For argon-methane mixtures the gas mul-

tiplication increases as the concentration of methane increases, reaches a maximum at a partial pressure of about 20 mm Hg, and then decreases. It is seen that the increase in the gas multiplication at a partial pressure of 20 mm Hg of methane is 20% at $V=700$, 60% at $V=1000$ and 480% at $V=1500$. It is now of interest to inquire why the presence of methane increases the gas multiplication, since the ionization potential of methane is 13.1 eV and is appreciably higher than the metastable potential of argon. (11.55 eV) Probably 11.55 volts can hardly be transferred to ionize methane molecule.

Table I.

V	600	700	800	1000	1500
$X/P)_{max}$	15.8	18.4	21.0	26.3	39.5
(α/P)	0.06	0.085	0.15	0.22	0.45
$(\alpha/P)_{Krutt.}$	0.038	0.062	0.11	0.155	0.425

The saturation current does not vary appreciably with the addition of methane, whereas the rise of the current at lower applied voltage (0~50 V) becomes slower.

For argon-ethane mixtures the behavior of the gas multiplication is similar to that for argon-methane mixtures, viz. it increases, reaches a maximum and then decreases with the addition of ethane. However the effect of ethane is more sensitive and the optimum pressure that gives a maximum gas multiplication is about 5 mm Hg. At this partial pressure of ethane, the increase in the gas multiplication is 380% at $V=700$, and 780% at $V=1000$.

On the basis of energy diagram the increase in the gas multiplication could be explained as the contribution of the second kind collision of the atoms, since the ionization potential of ethane is 11.6 eV and the defect of 0.05 eV could be supplied by their kinetic energies.

In passing, it is found that the region of ionization chamber operation becomes narrow and steep as the concentration of ethane increases. Moreover the saturation current increases appreciably, as is easily expected from the measurements of Melton et al on the average energy loss per ion pair by α -particles.

For argon-propane mixtures it is seen that

the degree of the increase in the gas multiplication with the addition of propane is more marked, and furthermore, the optimum pressure is about 1 mm Hg, which is less than those of above mentioned two gases. The gas multiplication at this partial pressure is about 32 times the value for pure argon at $V=700$.

With this more marked effectiveness of propane it is to be noted that the ionization potential of propane is 11.2 eV, thus the resonance defect ΔE between this and the metastable potential of argon is 0.35 eV and larger than that for argon-ethane.

For argon-normal butane mixtures the curves of ionization current are shown in Fig. 5. Quite similar curves are obtained also for argon-iso butane mixtures. The effect of traces of butane is more remarkable than those of above mentioned gases. The gas multiplication at a optimum partial pressure of 0.3 mm Hg of butane is about 80 times the value for pure argon at $V=700$.

The ionization potential of normal butane is 10.8 eV and the energy difference between this and the metastable potential of argon increases further.

Fig. 6 gives the ionization current for argon-normal pentane mixtures. Also for argon-iso pentane mixtures no appreciable difference is observed on the behavior of the gas multiplication. The effect of pentane on increasing the gas multiplication is most prominent among argon-alkanes mixtures investigated. Again, it is to be noted that the ionization potential of normal pentane is 10.55 eV and thus the the resonance defect increases further.

The conclusions to be drawn from our measurements on the ionization in argon-alkanes mixtures are then as follows.

(1) The gas multiplication increases when a small quantity any alkane gas is added to argon. By further addition, it reaches a maximum and then decreases.

(2) The degree of the gas multiplication at the presence of traces of alkane gas increases progressively in order of methane, methane, ethane, propane, butane and pentane. Recalling gradual reduction of the ionization potential in this order, this feature would have a bearing on the ionization potential of added gas.

(3) The optimum pressure that gives a maximum gas multiplication decreases in above mentioned order.

For convenience of direct comparison, the gas multiplication, i/i_0 , at $V=700$ is shown in Fig. 7. The values of the Townsend ionization coefficient in optimum mixtures of argon-alkanes and the values of optimum concentration are summarized in Table II.

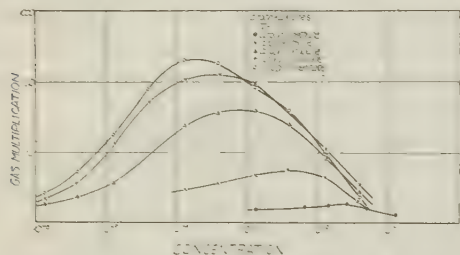


Fig. 7. Gas multiplication i/i_0 in argon-alkanes mixtures at $V=700$ as a function of the concentration of alkanes.

Table II.

	V_i	$C_{opt.}$	$\frac{\alpha}{P}$
C_2H_4	10.5	6.5×10^{-4}	0.31
C_3H_6	9.8	4×10^{-4}	0.33
$C_4H_8(1)$	9.7	4×10^{-4}	0.47
<i>cis</i> $C_4H_8(2)$	9.3	1.3×10^{-4}	0.25

3.2 Argon-Alkenes

Alkenes used in our investigation are ethylene, propylene, butene (1), *iso* butene, *trans*-butene (2) and *cis*-butene (2), among which *iso* butene and *trans*-butene (2) exhibit the curves closely resembling to those for *cis*-butene (2).

General tendency of the curves for these gas mixtures are similar to those for argon-alkanes. It is found that, as the concentration of alkenes is raised from small to large value, the gas multiplication rises and after passing a maximum it falls.

The effect of the impurities on increasing the gas multiplication advances orderly with alkene's number. This feature is also consistent with that for argon-alkanes, since the ionization potentials of alkenes are 10.5 eV for ethylene, 9.8 eV for propylene, 9.7 eV for butene (1) and 9.3 eV for *cis*-butene (2) and thus the increase seems mainly depend on the ionization potentials of added impurities.

Here again, we cannot observe a resonance between the added impurities and the metastable atoms of argon.

Moreover it is found that the optimum pressure of alkenes, though slightly, decreases in this order.

For direct comparison of above mentioned characteristics, the gas multiplication i/i_0 , at $V=700$ is plotted in Fig. 8. The values of the Townsend ionization coefficient at $X/P=1.58$ V/cm/mm Hg in optimum mixtures and the values of optimum concentration are shown in Table III.

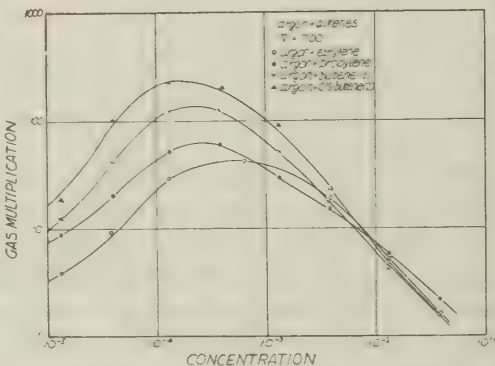


Fig. 8. Gas multiplication i/i_0 in argon-alkenes mixtures at $V=700$ as a function of the concentration of alkenes.

Table III.

	V_i	C_{opt}	$\frac{\alpha}{P}$
CH_4	13.1	2.6×10^{-2}	0.08
C_2H_6	11.6	4×10^{-3}	0.19
C_3H_8	11.2	1.3×10^{-3}	0.32
C_4H_{10}	10.8	4×10^{-4}	0.50
C_6H_{12}	10.55	4×10^{-4}	0.55

3.3 Argon-Alcohols

Alcohols used in our experiments are methyl alcohol, ethyl alcohol and *normal* propyl alcohol whose ionization potentials 10.8 eV, 10.6 eV and 10.4 eV respectively. The results obtained show that a small quantity of alcohols increases the gas multiplication in the same way as in above mentioned mixtures. However, quite the reverse is observed in the effect of admixtures in increasing the gas multiplication, that is, it decreases gradually in order of methyl alcohol, ethyl alcohol and propyl alcohol. Again, in these gas mixtures

resonance is not observed, since the resonance defect between the ionization potential of the impurity and the metastable potential of argon is minimum for argon-ethyl alcohol.

Fig. 9. shows the curves of the gas multiplication vs concentration of the impurities at $V=700$ and Table IV shows the values of the Townsend ionization coefficient at $X/P=15.8\text{V/cm/mm.Hg}$ in optimum mixtures and the values of optimum concentration.

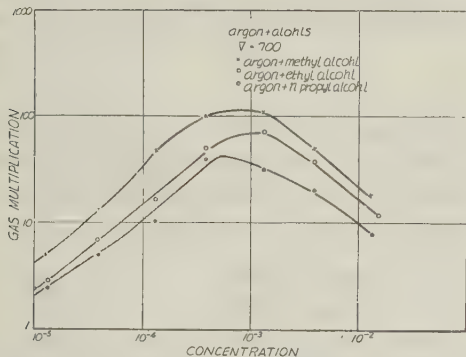


Fig. 9. Gas multiplication i/i_0 in argon-alcohols mixtures at $V=700$ as a function of the concentration of alcohols.

Table IV.

	V_t	C_{opt}	α/P
CH_3OH	10.8	1.3×10^{-3}	0.47
$\text{C}_2\text{H}_5\text{OH}$	10.6	1.3×10^{-3}	0.33
$\text{nC}_3\text{H}_7\text{OH}$	10.4	4×14^{-4}	0.30

3.4 Argon-Benzene, Argon-Acetylene

Fig. 10 shows the ionization current vs voltage for argon-benzene mixtures. Again, an increase in the ionization current is observed when a small amount of benzene is added to argon. The effect of benzene, however, is very sensitive, that is, the optimum par-pressure of benzene is as small as about 0.01 mm Hg and about 10 mm Hg of benzene almost suppresses the increase in ionization.

The ionization potential of benzene is 9.24 V and is about equal to that of *cis*-butene (2). The difference of the effect between two gases will be due to supposed difference between their ionization cross-sections.

Fig. 11 is the curves of the ionization current vs voltages for argon-acetylene mixtures. The optimum pressure of acetylene of

0.5 mm Hg gives greater gas multiplication than any other gas of optimum pressure investigated in our measurements. This is in accordance with the experiments of Melton al on energy loss by α -particles.

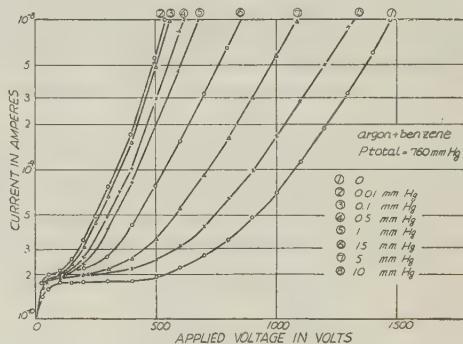


Fig. 10. Ionization current in argon-benzene mixtures at $P_{total}=760$ mm Hg. Partial pressure of benzene is indicated by the figures on the curves.

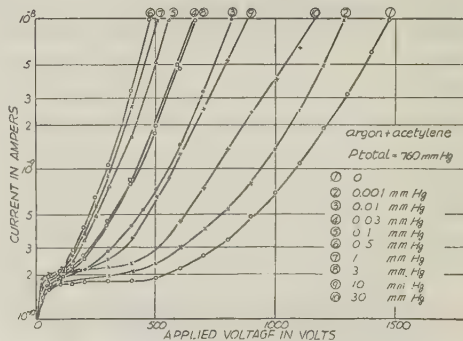


Fig. 11. Ionization current in argon-acetylene mixtures at $P_{total}=760$ mm Hg. Partial pressure of acetylene is indicated by the figures on the curves.

3.5 Argon-Krypton, Argon-Xenon

Inert gases lower ionization potential than that of argon are krypton and xenon. The values are 14 eV and 12.15 eV respectively.

Again, a small amount to krypton and xenon increases the gas multiplication when added to argon, as organic vapors do. The degree of the increase in ionization is more marked in the latter gas mixtures and the optimum pressures are about 100 mm Hg for krypton and about 10 mm Hg for xenon. This tendency coincides with those for argon-alkanes and argon-alkenes.

The appreciably higher ionization potentials of these gases than the metastable poten-

tial of argon suggest that Penning effect could not occur in these gas mixtures.

The curves of the gas multiplication vs concentration of krypton and xenon at $V=700$ are shown in Fig. 12. Table V shows the values of the Townsend ionization coefficient at $X/P=15.8$ V/cm/mmHg in optimum mixtures and the values of the optimum concentration.

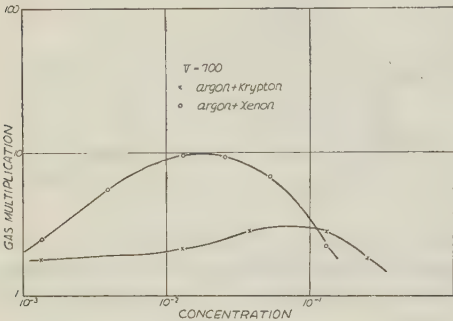


Fig. 12. Gas multiplication i/i_0 in argon-krypton and argon-xenon mixtures at $V=700$ as a function of the concentration of krypton and xenon.

Table V.

	V_i	$C_{opt.}$	α/P
Kr	14.0	1.3×10^{-1}	0.13
Xe	12.15	1.3×10^{-2}	0.29

§ 4. Townsend Ionization Coefficient in Argon-alkanes Mixtures

For the convenience of theoretical discussion, it is necessary to evaluate the Townsend ionization coefficient from our ionization curves. Our measurements are carried out in a convergent field and the determination of α in this field has been scarcely attempted, since α has a validity only when electric field does not vary appreciably in the range of electron mean free path. In our case filling pressure is one atmosphere and the length of electron mean free path is of order of 10^{-5} cm and is short enough to evaluate α .

Now in our coaxial cylindrical electrode system, a swarm of electrons starts an avalanche at a distance of critical $(X/P)_{crit.}$ near anode and proceeds down to the surface of the anode. Thus the gas multiplication is given by (1). Since $X/X_{m\infty}=a/x$, we find readily,

$$\frac{i}{i_0} = \exp \int_{(X/P)_{crit.}}^{(X/P)_{max}} aP \left(\frac{\alpha}{P}\right) \left(\frac{X}{P}\right)^{-2} \left(\frac{X}{P}\right)_{max} d\left(\frac{X}{P}\right) \tag{2}$$

or

$$\frac{1}{aP} \frac{1}{(X/P)_{max}} \ln \frac{i}{i_0} = \int_{(X/P)_{crit.}}^{(X/P)_{max}} \left(\frac{\alpha}{P}\right) \left(\frac{X}{P}\right)^{-2} d\left(\frac{X}{P}\right) \tag{3}$$

By differentiation with respect to $(X/P)_{max}$, we obtain

$$\frac{1}{aP} \left\{ \left(\frac{X}{P}\right)_{max} \frac{d}{d(X/P)_{max}} \ln \frac{i}{i_0} - \ln \frac{i}{i_0} \right\} = \left(\frac{\alpha}{P}\right)_{max} \tag{4}$$

This equation is quite the same as Johnsons fomula in a divergent field⁵⁾. Since the relation between maximum field strength and

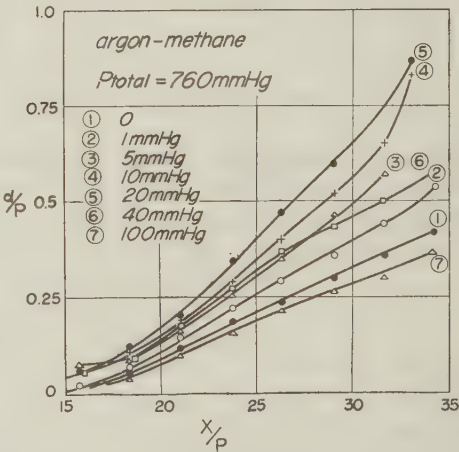


Fig. 13. Ionization coefficient α/p for argon-methane mixtures. $P_{total}=760$ mm Hg. Partial pressure of methane is indicated by the figures.

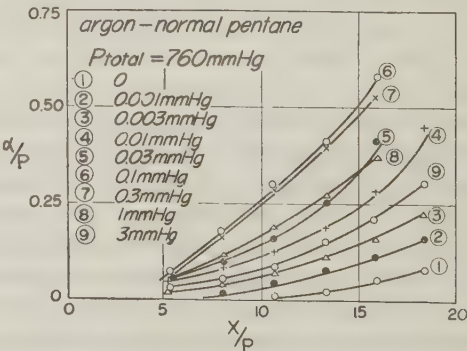


Fig. 14. Ionization coefficient α/p for argon-normal pentane mixtures. $P_{total}=760$ mm Hg. Partial pressure of pentane is indicated by the figures.

applied voltage is given by,

$$X_{\max.} = \frac{V}{\ln b/a} \quad (5)$$

Eq. (4) reduces to

$$\left(\frac{\alpha}{P}\right)_{m, \max} = \left(\frac{X}{P}\right)_{m, \max} \ln \frac{b}{a} \cdot \frac{1}{i} \frac{di}{dV} - \frac{1}{ap} \ln \frac{i}{i_0} \quad (6)$$

The values of the Townsend ionization coefficient obtained by means of (6) from the ionization curves in argon-alkanes mixtures are shown in Figs. 13-16.

production rate of G_{1met} there is an optimum amount of G_2 for G_{1met} to be completely removed.

Applying this mechanism to our results, there are two kinds of difficulty, as has been occasionally mentioned. First, it is difficult to explain the increase in ionization in mixtures of argon-methane, argon-krypton and argon-xenon. The metastable potential of argon is 11.55 eV and the ionization potentials of methane, krypton and xenon are 13.1 eV, 14 eV and 12.15 eV respectively and thus the condition $V_{1met} \geq V_{2i}$ is not satisfied. Next, the ionization rate, dn/dt , due to the metastable atoms will be given by,

$$\frac{dn}{dt} = n_{1met} \cdot n_2 qu \quad (7)$$

where n_{1met} is the density of the metastable atoms, n_2 that of the second gas, q cross-section of this process and u relative velocity between the colliding atoms. The cross-section of the energy transfer of excitation energy between atoms on collision has been known to be of resonance type, as Morse and Stueckelberg⁶⁾ made a detailed calculation for the second kind collision. The probability of this energy transfer is maximum when the resonance defect ΔE is zero. Therefore, for a given production rate of the metastable atoms an optimum quantity of any added gas will give about the same ionization and the least quantity is needed when $\Delta E = 0$.

On the basis of above discussion it is impossible to explain the results of a series of our measurements. In argon-alkanes mixtures the resonance defect is least for argon-ethane mixture, whereas our results show the gradual decrease in optimum quantity and the gradual increase in ionization with the continual reduction of the ionization potentials of added gases. In argon-alkenes mixtures the resonance defect is least for argon-ethylene mixture, whereas our results are about the same for argon-alkanes. Again in argon-alcohols mixtures, the resonance phenomena is not observed.

However, these difficulties of the Penning effect are expected from the experiment of A. H. Futch and F. A. Grant⁷⁾ on the mean life of $^3P_2$ metastable argon atoms. The mean life of $^3P_2$ metastable argon due to the destruction by three body collision was given by,

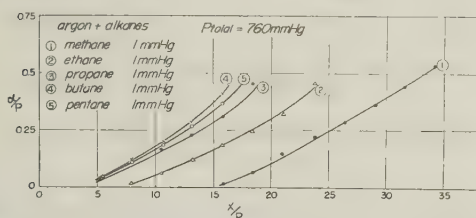


Fig. 15. Ionization coefficient α/p for argon-alkanes mixtures. $P_{total} = 760$ mm Hg. Partial pressure of alkanes is 1 mm Hg.

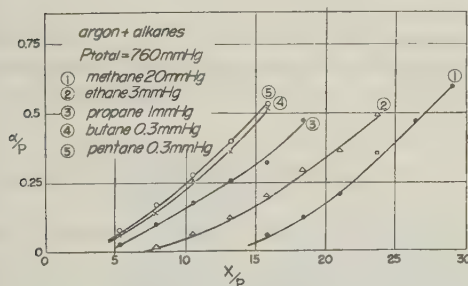


Fig. 16. Ionization coefficient α/p for optimum argon-alkanes mixtures. $P_{total} = 760$ mm Hg. Optimum partial pressure of alkanes in indicated by the figures.

§ 5. Discussions

5.1 Penning effect

According to generally accepted Penning effect, electrons in collision with gas atoms G_1 such as neon atoms, may excite the atoms, leave them in the metastable states G_{1met} which at the presence of a small amount of the second gas G_2 , ionize the latter. This process will occur provided that the ionization potential V_{2i} of the second gas is less than, but close to the potential V_{1met} of the metastables G_{1met} .

Furthermore it is assumed that for a given

$$\tau = \frac{1}{13.5p^2} \quad (8)$$

where p is pressure in mmHg. In our case of $p=760$ mmHg, $\tau \approx 1.3 \times 10^{-7}$ sec. The frequency of collision of a metastable argon atom with impurity gas of partial pressure of 1 mmHg is about 10^5 /sec, and thus only 1% of metastable atoms could collide with impurity atoms during the mean life time.

5.2 Direct impact ionization

The Townsend ionization coefficient can be easily obtained, provided that electron distribution is assumed to be Maxwellian, and is given by,

$$\alpha = a_1 n_1 \frac{1}{\sqrt{f}} \sqrt{\frac{4}{\pi}} e^{-V_{i1}/V_e} (V_{i1} + V_e) + a_2 n_2 \frac{1}{\sqrt{f}} \sqrt{\frac{4}{\pi}} e^{-V_{i2}/V_e} (V_{i2} + V_e) \quad (9)$$

where a is the initial slope of the ionization cross-section, n the density of the gas, f the average fractional loss of electron energy per collision, V_i ionization potential of the gas, V_e mean energy of electrons. The second term represents the contribution of the added impurity gas and is expected from Fig. 17 to become more effective as the ionization potential of the impurity lowers. For the numerical evaluation of this term, we use Townsend and Baileys data⁹⁾ relating average electron energy and loss factor to the ratio X/P . In argon at $X/P=15$ V/cm/mmHg, $V_e=11.1$ eV and $f=33.8 \times 10^{-4}$. Assuming that $a_1 \approx a_2$, the ratios of the second term to the first in optimum mixtures are 3.1×10^{-2} for methane, 5.8×10^{-3} for ethane,

1.5×10^{-3} for propane, 6.3×10^{-4} for butane and 3.2×10^{-4} for pentane respectively. The agreement is quite unsatisfactory. But this disagreement is not unexpected, for it has been mentioned that theoretical values of α/P in argon are from two to four orders of magnitude too high and thus the distribution curve in argon should fall off very much steeply than Maxwellian with increase in energy above about the mean energy⁹⁾.

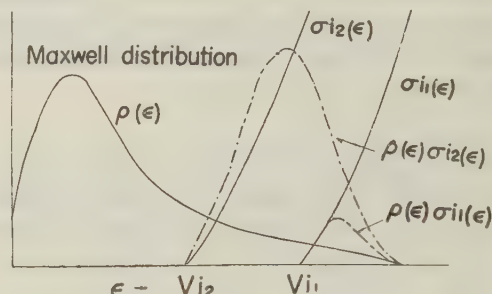


Fig. 17. Graphical illustration of direct impact ionization in a mixture gas. ρ : electron energy distribution. σ_{i1} : ionization cross-section of the main gas. σ_{i2} : ionization cross-section of the impurity gas.

Therefore the actual electron distribution curve in argon would be of following form, as proposed by H. D. Deas and K. G. Emeleus¹⁰⁾

$$F(V) = A_k V^{1/2} \exp \left\{ - \left(c \frac{V}{V_e} \right)^k \right\} \quad (10)$$

Applying this distribution function, the Townsend ionization coefficient is given by the incomplete gamma function, which is approximately expressed by,

$$\alpha = \frac{n_1 a_1 V_{i1}}{\sqrt{f} \sqrt{\Gamma(5/2k) \Gamma(3/2k)}} \frac{1}{k} \left(c \frac{V_{i1}}{V_e} \right)^{2-2k} \exp \left\{ - \left(c \frac{V_{i1}}{V_e} \right)^k \right\} + \frac{n_2 a_2 V_{i2}}{\sqrt{f} \sqrt{\Gamma(5/2k) \Gamma(3/2k)}} \frac{1}{k} \left(c \frac{V_{i2}}{V_e} \right)^{2-2k} \exp \left\{ - \left(c \frac{V_{i2}}{V_e} \right)^k \right\} \quad (11)$$

For the arbitrary choice of $k=8$, the ratios of the second term to the first in optimum mixtures are 3.2×10^2 for methane, 4.0×10^2 for ethane, 2.5×10^2 for propane, 1.2×10^2 for butane, and 2.0×10^2 for pentane respectively. The contribution of the impurities to an increase in ionization is sufficiently large compared with that of the main gas.

Let us next discuss briefly the optimum

quantity relating to the direct impact process. The addition of that impurity will give rise to an increase in ionization in above mentioned manner, whereas it will reduce electron mean energy due to supposed larger value of the loss factor of the impurity. The electron mean energy is given by

$$V_e = \sqrt{\frac{\pi}{8}} \frac{\lambda X}{\sqrt{f}} \quad (12)$$

In the case of small admixture, λ will not change substantially, and it is sufficient to take into account the variation of f . Evidently the loss factor in mixture gases is the average of those for the component gases and is expressed by

$$f = \frac{S_1 n_1}{S n} f_1 + \frac{S_2 n_2}{S n} f_2 \approx f_1 + \frac{S_2 n_2}{S_1 n} f_2 \tag{13}$$

where
 S =average collision cross-section in mixture gases
 $S_{1,2}$ =corresponding quantities of the components.

Substituting (13) in (12) we obtain in approximation that

$$\begin{aligned} V_e &= \sqrt{\frac{\pi}{8}} \frac{\lambda X}{\sqrt{f_1}} \left(1 - \frac{1}{2} \frac{S_2 f_2}{S_1 f_1} \frac{n_2}{n}\right) \\ &= V_{e0} \left(1 - \frac{1}{2} \frac{S_2 f_2}{S_1 f_1} \frac{n_2}{n}\right) \end{aligned} \tag{14}$$

where V_{e0} is the mean energy in pure main gas. Eq. (14) represents linear decrease in the electron mean energy as a function of the concentration of the impurity gas and the degree of the decrease is proportional to the ratio of the loss factor multiplied by the cross-section.

Substituting (14) in the second term of (11), we obtain that

$$\begin{aligned} \frac{\alpha}{n} &\approx \frac{n_2 a_2 V_{e0}}{n \sqrt{\Gamma(5/2k)\Gamma(3/k)}} \frac{1}{k} \left(c \frac{V_{e0}}{V_{e0}}\right)^{2-2k} \\ &\exp \left\{ - \left(c \frac{V_{e0}}{V_{e0}}\right)^k \left(1 + \frac{k}{2} \frac{S_2 f_2 n_2}{S_1 f_1 n}\right) \right\} \end{aligned} \tag{15}$$

This formula expresses that α/n increases with concentration of the impurity, reaches a maximum at a value of

$$\left(\frac{n}{n}\right)_{max} \approx \left(\frac{V_{e0}}{c V_{e0}}\right)^k \frac{2}{k} \frac{S_1 f_1}{S_2 f_2} \tag{16}$$

and then decreases.
Theoretical result of optimum quantity given by (16) represents that this quantity depends mainly on the ratio $S_1 f_1 / S_2 f_2$, since V_{e0} / V_{e0} is of order of unity. In alkanes it will be supposed that the loss-factor f_2 and the cross-section S_2 will become greater with increasing chain of alkanes. Thus the gradual decrease of this quantity in this order is quite a satisfactory agreement qualitatively.

The weakness of the direct impact ionization process is an arbitrary assumption of

electron distribution function, and thus for more thorough discussion it is necessary to determine an accurate distribution function.

5.3 Photoionization

The existence of photoinization in discharges of argon-organic vapor mixtures has been believed from the experiments of Geiger counters.

The spectra of argon in the region of extreme ultraviolet was investigated by J. C. Boyce¹¹⁾ and in spark discharge two lines with sufficient intensity (1066.66Å, 1048, 22Å) and four weak lines (894.3Å, 876.06Å, 869.75Å, 866.80Å) were observed. These spectra are emitted by transitions from states 4s, 5s and 3d to ground state. Photons corresponding to two intense lines with energies of 11.6 eV and 11.8 eV can ionize propane, butane and pentane and those corresponding four weak lines having energies of 13.8 eV, 14.1 eV, 14.2 eV and 14.3 eV can ionize also methane and ethane.

Production of these photons per cm path in the direction of field will be expressed by,

$$\begin{aligned} \omega &= \frac{na}{\sqrt{f}} \frac{V_{e0}}{\sqrt{\Gamma(5/2k)\Gamma(3/2k)}} \frac{1}{k} \left(c \frac{V_{ex}}{V_e}\right)^{2-2k} \\ &\exp \left\{ c \frac{V_{ex}}{V_e} \right\}^k \end{aligned} \tag{17}$$

where V_{ex} = the excitation potential. When we assume $k=8$, and that the slope of the excitation cross-section is nearly equal to that of the ionization cross-section, the ratio ω/α will reach about 2×10^4 for $V_{ex}=11.5$ eV and 5×10^2 for $V_{ex}=14$ eV.

As to the values of the absorption coefficient for photo-ionization of organic vapors, data are available only for methane, ethylene and acetylene¹²⁾. The value of the cross-section for methane at $\lambda=850$ Å are about 1.5×10^{-17} cm², and those for ethylene and acetylene at $\lambda=1050$ Å are about 2×10^{-17} cm². From the absorption formula $\exp(-\sigma N P x)$, about a half of these photons is absorbed by these addition gases at partial pressure of 1 mmHg, and thus the effect of photoionization cannot be neglected.

In conclusion of above discussions, it seems clear that the increase in ionization in argon mixtures at higher pressure will be ascribed partly to direct impact ionization and partly to photoionization. The investigation on the low pressure discharge in mixture gases is

contemplated for the future to make clear as yet ambiguous points.

The author wishes to express his sincere thanks to Professor K. Honda and Dr. H. Tamagawa for their helpful discussions and to Mr. I. Makino, Dr. M. Sugawara and Dr. J. Nakamura for their kind guidance throughout the experiments.

References

- 1) A. A. Kruithoff and F. M. Penning: *Physica* **4** (1937) 430
- 2) F. M. Penning: *Phil. Mag* **11** (1931) 961; *Z. Phys.* **57** (1929) 723; *Physica* **11** (1931) 723
- 3) T. Nakaya: *J. Phys. Soc. Japan* **11** (1956) 1264
- 4) C. E. Melton, S. G. Hurst and T. E. Bortner: *Phys. Rev.* **96** (1954) 643
- 5) C. W. Johnson: *Phys. Rev.* **73** (1948) 283
- 6) P. M. Morse and E. C. G. Stueckelberg: *Ann. Physik* **9** (1931) 579
- 7) A. H. Futch and F. A. Grant: *Phys. Rev.* **104** (1956) 356
- 8) L. B. Loeb: *Basic Processes of Gaseous Electronics* (Univ. California Press, 1955) 368
- 9) L. B. Loeb: *idib.* 322
- 10) H. D. Deas and K. G. Emeleus: *Phil. Mag.* **40** (1949) 460
- 11) J. C. Boyce: *Phys. Rev.* **48** (1935) 396
- 12) G. L. Weissler: *Handbuch der Physik* **XXI** (Springer-verlag, 1956) 304

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Non-linear Effects on Electron-Plasma Oscillations

By Masao SUMI

*Electrical Communication Laboratory,
Musashino-shi, Tokyo, Japan.*

(Received February 4, 1960)

Non-linear effects are investigated in the excitation of electron-plasma oscillations, by considering a non-linear term in the Boltzmann equation as a perturbation. With the growth of fundamental component, the second and the higher harmonics are generated as forced oscillations. The magnitudes of these components are estimated which give the criteria of validity of linear approximation. Finally the behaviours of excited waves in the limit of large amplitude are described.

§ 1. Introduction

The linear theory of electron-oscillations excited by the interaction between a plasma medium and a traversing electron beam has already been investigated in some detail by the same author.¹⁾⁻⁴⁾ The increase of oscillating amplitude beyond the linear approximation will give rise to some non-linear effects. This paper will mainly deal with the genesis and characteristics of these effects.

A number of papers on non-linear plasma oscillations have since been published,⁵⁾⁻¹⁵⁾ but most of them have not treated the excitation mechanism explicitly. In some works only a final state with large stationary ampli-

tude has been considered in the presence of interacting electron beams, and hence the process of generation of higher harmonics involved has not been discussed.

In the present article we shall deal with a non-linear term in the fundamental equations, as a perturbation and examine non-linear effects which will cause appreciable corrections to consequences obtained by the linear theory. Higher harmonics and the higher-order corrections to fundamental component will be calculated by means of successive approximation. In the limit of wave-growth the oscillation amplitude will be expected to attain a saturation level.

§ 2. Fundamental Equations

We shall not intend here general considerations of non-linear effects, but restrict ourselves to the following case. 1) Ions are regarded as a uniform background of positive charge. 2) The effect of short-range collisions on the oscillation is neglected. 3) No static fields are present. 4) We consider only one-dimensional case. 5) Electrons are divided into two groups: one constituting a plasma-medium and the other running to form a beam. 6) Waves, growing up in time or in space as a result of interaction between two electron-groups, are supposed to have, respectively, a definite wave-number or frequency. Hence only coherent oscillations are considered and incoherent or noisy components are discarded for the present.

Fundamental equations are the Boltzmann equation for the distribution function of electron-velocity and the Poisson equation satisfied by the oscillating electric field arising from long-range correlations between electrons. Under the assumptions made in the last paragraph they are written as

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} - \frac{e}{m} E \frac{\partial f_0}{\partial v} = \frac{e}{m} E \frac{\partial f}{\partial v}, \quad (2.1)$$

$$\frac{\partial E}{\partial x} = -\frac{e}{\partial x} \int f dv, \quad (2.2)$$

where f_0 is a stationary part of the distribution function and f its oscillating one.

First a wave excited in time will be examined, and a wave growing in space will be discussed in a later section.

The functions f and E are Fourier-analysed in a unit interval of space. Hence

$$f = \sum_k f_k e^{ikx}, \quad E = \sum_k E_k e^{ikx}.$$

The summation extends over all values of k which are integral multiples of 2π . Since f and E are real, the following relations result

$$f_{-k} = f_k^*, \quad E_{-k} = E_k^*,$$

where the asterisk denotes the complex conjugate of respective quantity. Then (2.1) and (2.2) become

$$\frac{\partial f_k}{\partial t} + ikvf_k - \frac{e}{m} E_k \frac{\partial f_0}{\partial v} = \frac{e}{m} \sum_{k'} E_{k'} \frac{\partial f_{k-k'}}{\partial v}, \quad (2.3)$$

$$ikE_k = -\frac{e}{\epsilon_0} \int f_k dv. \quad (2.4)$$

The right-hand side of (2.3) represents the non-linear term in this problem. In order to

regard this term as a perturbation, we introduce a parameter λ for convenience to write it

$$\lambda \frac{e}{m} \sum_{k'} E_{k'} \frac{\partial f_{k-k'}}{\partial v}.$$

According to the usual procedure of perturbation method, we put

$$\left. \begin{aligned} f_k &= f_k^{(0)} + \lambda f_k^{(1)} + \lambda^2 f_k^{(2)} + \dots, \\ E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots \end{aligned} \right\} \quad (2.5)$$

Inserting these into (2.3) and (2.4) and taking terms of the same power with respect to λ , we get the series of following equations in the successive approximation. Here it should be noted that by virtue of the assumption 6) only a wave with a definite wave-number has a considerable amplitude and therefore another wave-component becomes negligible at the stage of linear approximation. As a result, we can greatly simplify the non-linear terms and obtain

zeroth-order equations:

$$\left. \begin{aligned} \frac{\partial f_k^{(0)}}{\partial t} + ikvf_k^{(0)} - \frac{e}{m} E_k^{(0)} \frac{\partial f_0}{\partial v} &= 0, \\ ikE_k^{(0)} &= -\frac{e}{\epsilon_0} \int f_k^{(0)} dv, \end{aligned} \right\} \quad (2.6)$$

first-order equations:

$$\left. \begin{aligned} \frac{\partial f_{2k}^{(1)}}{\partial t} + 2ikvf_{2k}^{(1)} - \frac{e}{m} E_{2k}^{(1)} \frac{\partial f_0}{\partial v} &= \frac{e}{m} E_k^{(0)} \frac{\partial f_k^{(0)}}{\partial v}, \\ 2ikE_{2k}^{(1)} &= -\frac{e}{\epsilon_0} \int f_{2k}^{(1)} dv, \end{aligned} \right\} \quad (2.7)$$

second-order equations:

$$\left. \begin{aligned} \frac{\partial f_{3k}^{(2)}}{\partial t} + 3ikvf_{3k}^{(2)} - \frac{e}{m} E_{3k}^{(2)} \frac{\partial f_0}{\partial v} \\ = \frac{e}{m} \left(E_{2k}^{(1)} \frac{\partial f_k^{(0)}}{\partial v} + E_k^{(0)} \frac{\partial f_{2k}^{(1)}}{\partial v} \right), \\ 3ikE_{3k}^{(2)} &= -\frac{e}{\epsilon_0} \int f_{3k}^{(2)} dv, \end{aligned} \right\} \quad (2.8)$$

and

$$\left. \begin{aligned} \frac{\partial f_k^{(2)}}{\partial t} + ikvf_k^{(2)} - \frac{e}{m} E_k^{(2)} \frac{\partial f_0}{\partial v} \\ = \frac{e}{m} \left(E_{2k}^{(1)} \frac{\partial f_{-k}^{(0)}}{\partial v} + E_{-k}^{(0)} \frac{\partial f_{2k}^{(1)}}{\partial v} \right), \\ ikE_k^{(2)} &= -\frac{e}{\epsilon_0} \int f_k^{(2)} dv, \end{aligned} \right\} \quad (2.9)$$

third-order equations:

We know that zeroth-order equations provide the linear approximation of the funda-

mental wave, first-order ones second harmonics and second-order equations third harmonics and the correction to fundamental wave.

§ 3. Fundamental and Harmonic Waves

The fundamental wave is obtained in the linear approximation by solving (2.6). As was discussed in the preceding work,¹⁾ excited waves exist for the suitable distribution function f_0 . When a growing wave becomes enough large to neglect transient effects, it may be written as

$$E_k^{(0)} = E_k(0)e^{-i\omega t}, \quad (3.1)$$

where $\omega = \omega_0 + i\gamma$, γ being positive. Thus the wave increases proportionally to $\exp(\gamma t)$. ω and k are connected with each other by the dispersion relation

$$I_0 \equiv \frac{e^2}{m\epsilon_0} \int \frac{f}{(\omega - kv)^2} dv = 1. \quad (3.2)$$

It is known that the wave-number k of excited wave, in general, takes any value within a certain range. However, if a wave with a single value of k is strongly excited, as is realized in the plasma-layer,¹⁾²⁾ the oscillating part of distribution function becomes

$$f_k^{(0)} = \frac{ie}{m} \frac{\partial f_0 / \partial v}{(\omega - kv)} E_k(0) e^{-i\omega t}. \quad (3.3)$$

When the wave grows up in the quiescent plasma-medium, the initial field $E_k(0)$ corresponds to a thermal level of plasma oscillations.

Next we can get the second harmonics from (2.7). The non-linear term of this equation is represented by the fundamental wave of linearized theory, say, by (3.1) and (3.3). Thus it varies with time as $\exp(-2i\omega t) = \exp(2\gamma t) \exp(-2i\omega_0 t)$. The increase of this term brings about the second-harmonic component as a forced oscillation, resulting its electric field

$$E_{2k}^{(1)} = -\frac{iek}{m\omega_p^2} I_2 (E_k^{(0)})^2, \quad (3.4)$$

where I_2 stands for the integration

$$I_2 \equiv \frac{\omega_p^2 e^2}{m\epsilon_0} \int \frac{f_0}{(\omega - kv)^4} dv,$$

and $\omega_p^2 = n_p e^2 / m\epsilon_0$, n_p being the number density of plasma-medium.

In a similar manner the third harmonics is obtained from (2.8), which gives

$$E_{3k}^{(2)} = -\frac{3}{16} \left(\frac{ek^2}{m\omega_p^2} \right)^2 (3I_2^2 + 5I_4) (E_k^{(0)})^3, \quad (3.5)$$

where

$$I_4 \equiv \frac{\omega_p^4 e^2}{m\epsilon_0} \int \frac{f_0}{(\omega - kv)^6} dv.$$

If we proceed to higher-order equations, we could calculate the fourth, the fifth harmonics and so on. In general, it is shown that the m -th harmonics is proportional to $(E_k^{(0)})^m$.

The second-order correction term of fundamental wave is given by the solution of (2.9). Considering the time factor $\exp(3\gamma t) \exp(-i\omega_0 t)$ of the non-linear term, we get a result of a form

$$E_k^{(2)} = \left(\frac{ek^2}{m\omega_p^2} \right)^2 \frac{\{I_2 G_2 - \frac{1}{2}(I_2 G_2' + I_4')\}}{(1 - I_0')} |E_k^{(0)}|^2 \cdot E_k^{(0)}, \quad (3.6)$$

where

$$\begin{aligned} I_0' &\equiv \frac{e^2}{m\epsilon_0} \int \frac{f_0}{(\omega - kv + 2i\gamma)^2} dv, \\ G_2 &\equiv \frac{\omega_p^2 e^2}{m\epsilon_0} \left[2 \int \frac{f_0}{(\omega - kv + 2i\gamma)^3 (\omega^* - kv)} dv \right. \\ &\quad \left. + \int \frac{f_0}{(\omega - kv + 2i\gamma)^2 (\omega^* - kv)^2} dv \right], \\ G_2' &\equiv \frac{\omega_p^2 e^2}{m\epsilon_0} \left[2 \int \frac{f_0}{(\omega - kv + 2i\gamma)^3 (\omega - kv)} dv \right. \\ &\quad \left. + \int \frac{f_0}{(\omega - kv + 2i\gamma)^2 (\omega - kv)^2} dv \right], \\ I_4' &\equiv \frac{3\omega_p^4 e^2}{m\epsilon_0} \left[\int \frac{f_0}{(\omega - kv + 2i\gamma)^2 (\omega - kv)^4} dv \right. \\ &\quad \left. + 2 \int \frac{f_0}{(\omega - kv + 2i\gamma)^3 (\omega - kv)^3} dv \right. \\ &\quad \left. + 2 \int \frac{f_0}{(\omega - kv + 2i\gamma)^4 (\omega - kv)^2} dv \right]. \end{aligned}$$

§ 4. Evaluations of Higher-order Components

Higher-order components represented by (3.4)–(3.6) can be evaluated most easily in the case where the number density of electrons in the plasma-medium n_p is of the same order of magnitude of that in the beam n_b . Then it is shown that integrals I_2 , I_4 , I_0' , G_2 , G_2' and I_4' are all of the order of magnitude unity.

Denoting $n_k = \int f_k dv$, we get

$$kE_k^{(0)} \sim \frac{en_k}{\epsilon_0}.$$

Thus (3.4) gives

$$\frac{E_{2k}^{(1)}}{E_k^{(0)}} \sim \frac{n_k}{n_p} \tag{4.1}$$

Similarly from (3.5) and (3.6), we find

$$\frac{E_{3k}^{(2)}}{E_k^{(0)}} \sim \frac{E_k^{(2)}}{E_k^{(0)}} \sim \left(\frac{n_k}{n_p}\right)^2 \tag{4.2}$$

Writing higher harmonic components of density as $n_{2k} = \int f_{2k} dv$ and $n_{3k} = \int f_{3k} dv$, we get from (4.1) and (4.2),

$$\frac{n_{2k}}{n_p} \sim \left(\frac{n_k}{n_p}\right)^2, \quad \frac{n_{3k}}{n_p} \sim \left(\frac{n_k}{n_p}\right)^3 \tag{4.3}$$

As for the m -th harmonics, in general, we can write as

$$\frac{E_{mk}^{(m-1)}}{E_k^{(0)}} \sim \left(\frac{n_k}{n_p}\right)^{m-1}, \quad \frac{n_{mk}}{n_p} \sim \left(\frac{n_k}{n_p}\right)^m \tag{4.4}$$

Next consider the case where the value of density ratio, $\sigma = n_b/n_p$, is far from unity. Then it is necessary to discriminate the group of electrons in the plasma-medium from that in the beam. The reason is that the non-linear effects on oscillations of one group are expected to be different from those of another. Thus fundamental equations (2.3) and (2.4) are replaced by the following three equations

$$\frac{\partial f_{kp}^p}{\partial t} + ikvf_{kp}^p - \frac{e}{m} E_k \frac{\partial f_0^p}{\partial v} = \frac{e}{m} \sum_{k'} E_{k'} \frac{\partial f_{k-k'}^p}{\partial v}, \tag{4.5}$$

$$\frac{\partial f_{kb}^b}{\partial t} + ikvf_{kb}^b - \frac{e}{m} E_k \frac{\partial f_0^b}{\partial v} = \frac{e}{m} \sum_{k'} E_{k'} \frac{\partial f_{k-k'}^b}{\partial v}, \tag{4.6}$$

$$ikE_k = -\frac{e}{\epsilon_0} \int (f_{kp}^p + f_{kb}^b) dv \tag{4.7}$$

Superscript p or b indicates the component for plasma-medium or beam, respectively. By means of the perturbation method developed in §2, we can derive the system of equations of each order from (4.5)–(4.7). Electric field components $E_k^{(0)}$, $E_{2k}^{(1)}$ and $E_{3k}^{(2)}$ obtained from these equations are the same as those in §2. Therefore the remaining task is to find $f_{kp}^p, f_{kb}^b; f_{2k}^p, f_{2k}^b; \dots$ by use of above equations. In what follows, we assume the distribution functions

$$\begin{aligned} f_0^p &= n_p (m/2\pi\kappa T)^{1/2} \exp(-mv^2/2\kappa T), \\ f_0^b &= n_b \delta(v - v_b), \end{aligned} \tag{4.8}$$

where v_b is the electron-velocity in the beam.

We shall consider only the case where $v_T = (2\kappa T/m)^{1/2}$ is negligible compared with v_b .

Corresponding to (3.3), the linear approximation of f_k^p becomes

$$f_k^p = \frac{ie}{m(\omega - kv)} \frac{\partial f_0^p}{\partial v} E_k(0) e^{-i\omega t} \tag{4.9}$$

Since the phase velocity of the excited wave is comparable with the beam velocity, using (4.8) and the assumption that $v_T \ll v_b$, we get

$$n_k^p = \int f_k^p dv = \frac{ek^2 n_p}{m\omega^2} V_k(0) e^{-i\omega t}, \tag{4.10}$$

where $E_k(0)$ is replaced by $V_k(0)$, by means of the relation: $E_k(0) = \partial V_k(0)/\partial x = ikV_k(0)$. Thus the electric potential arising from electrons in the plasma-medium is

$$V_k^p = \frac{e}{\epsilon_0 k^2} n_k^p = \frac{\omega_p^2}{\omega^2} V_k(0) e^{-i\omega t}, \tag{4.11}$$

Corresponding quantities for the beam are written as

$$n_k^b = \frac{ek^2 n_b}{m(\omega - kv_b)^2} V_k(0) e^{-i\omega t}, \tag{4.12}$$

and

$$V_k^b = \frac{\omega_b^2}{(\omega - kv_b)^2} V_k(0) e^{-i\omega t}, \tag{4.13}$$

where $\omega_b^2 = n_b e^2 / m\epsilon_0$. The total potential becomes naturally

$$V_k = V_k^p + V_k^b = V_k(0) e^{-i\omega t},$$

with the aid of the dispersion relation for this case.

As for the second harmonics, we obtain

$$f_{2k}^p = \frac{ie}{2m(\omega - kv)} \left(E_{2k}^{(1)} \frac{\partial f_0^p}{\partial v} + E_k^{(0)} \frac{\partial f_k^p}{\partial v} \right),$$

and the similar expression for the beam component f_{2k}^b . These functions are integrated over the velocity space, yielding n_{2k}^p and n_{2k}^b . Then the ratios of the second harmonics to the fundamental component are given by

$$\frac{n_{2k}^p}{n_k^p} = -\frac{1}{2} \left(\frac{\omega^2}{\omega_p^2} I_2 + 3 \right) \left(\frac{\omega_p}{\omega} \right)^4 \frac{n_k^p}{n_p} (1 + \sigma_k)^2, \tag{4.14}$$

$$\begin{aligned} \frac{n_{2k}^b}{n_k^b} &= -\frac{1}{2} \left[\frac{(\omega - kv_b)^2}{\omega_p^2} I_2 + 3 \right] \\ &\times \left(\frac{\omega_b}{\omega - kv_b} \right)^4 \frac{n_k^b}{n_b} \left(1 + \frac{1}{\sigma_k} \right)^2, \end{aligned} \tag{4.15}$$

where $\sigma_k = n_k^b/n_k^p$.

In order to find conditions for which the linear theory is valid, we have to evaluate ratios $|n_k^p|/n_p$ and $|n_k^b|/n_b$. Then (4.10) and (4.12) give

$$\frac{|n_k^p|}{n_p} = \frac{ek^2 V_k(0)}{m|\omega|^2} e^{\gamma t} = \left(\frac{kv_b}{|\omega|} \right)^2 r(t),$$

$$\frac{|n_k^b|}{n_b} = \frac{ek^2 V_k(0)}{m|\omega - kv_b|^2} e^{\gamma t} = \left(\frac{kv_b}{|\omega - kv_b|} \right)^2 r(t),$$

where

$$r(t) \equiv \frac{e V_k(0) e^{\gamma t}}{m v_b^2}. \quad (4.16)$$

Now using (A.6) and (A.8) in the Appendix we find for $\sigma^{1/3} \ll 1$

$$\frac{|n_k^p|}{n_p} \sim r(t), \quad \frac{|n_k^b|}{n_b} \sim \frac{r(t)}{\sigma^{2/3}}, \quad (4.17)$$

and for $\sigma^{1/3} \gg 1$

$$\frac{|n_k^p|}{n_p} \sim \sigma^{2/3} r(t), \quad \frac{|n_k^b|}{n_b} \sim r(t). \quad (4.18)$$

Before evaluating further, the ratio of oscillating densities are required

$$\sigma_k = \frac{\omega_b^2 (\omega - kv_b)^2}{\omega_p^2 \omega^2} \sim \sigma^{2/3}, \quad (4.19)$$

where σ may take any value. Making use of this and (A.6), (A.8) and (A.9), the ratios (4.14) and (4.15) are estimated for $\sigma^{1/3} \ll 1$

$$\left| \frac{n_{2k}^p}{n_k^p} \right| \sim \frac{r(t)}{\sigma^{1/3}}, \quad \left| \frac{n_{2k}^b}{n_k^b} \right| \sim \frac{r(t)}{\sigma^{2/3}}, \quad (4.20)$$

and for $\sigma^{1/3} \gg 1$

$$\left| \frac{n_{2k}^p}{n_k^p} \right| \sim \sigma^{2/3} r(t), \quad \left| \frac{n_{2k}^b}{n_k^b} \right| \sim \sigma^{1/3} r(t). \quad (4.21)$$

Thus from (4.19) and (4.12), we obtain the ratio

$$\sigma_{2k} \equiv \frac{n_{2k}^b}{n_{2k}^p} \sim 1 \quad (4.22)$$

for all values of σ .

§ 5. Conditions of Linear Approximation and Behaviours at Large Amplitude

The inspection of the estimations in the last section will lead at once to the conditions for the validity of linear approximation, which can be written as

$$r(t) \ll \begin{cases} \sigma^{2/3} \\ 1 \\ \sigma^{-2/3} \end{cases}, \quad (5.1)$$

according to, respectively,

$$\begin{aligned} &\ll \\ \sigma^{1/3} &\sim 1. \\ &\gg \end{aligned}$$

For all cases above, in fact, we have

$$\begin{aligned} n_p &\gg |n_k^p| \gg |n_{2k}^p|, \\ n_b &\gg |n_k^b| \gg |n_{2k}^b|. \end{aligned} \quad (5.2)$$

If the oscillating amplitude becomes larger, resulting

$$r(t) \sim \sigma^{2/3} \text{ for } \sigma^{1/3} \ll 1, \quad (5.3)$$

we find instead of (5.2)

$$\begin{aligned} n_p &\gg |n_k^p| \gg |n_{2k}^p|, \\ n_b &\sim |n_k^b| \sim |n_{2k}^b|. \end{aligned} \quad (5.4)$$

This implies that, when the electron density in the beam is very much lower than that in the plasma, the beam is bunched almost completely and hence very rich at harmonics, while the plasma is still at the small-amplitude level. In other words, at this level the wave in the plasma can be treated by the linear theory and the modulation in the beam must be described by the non-linear theory.

For $\sigma^{1/3} \gg 1$, if $r(t) \sim \sigma^{-2/3} \ll 1$, we get similarly

$$\begin{aligned} n_p &\sim |n_k^p| \sim |n_{2k}^p|, \\ n_b &\gg |n_k^b| \gg |n_{2k}^b|. \end{aligned} \quad (5.5)$$

This shows just reverse situations to (5.4). The bunching of electrons is then strong in the plasma and weak in the beam.

The state represented by either (5.4) or (5.5) would correspond to the saturation level, which will be discussed in the following.

Consider a state given by (5.4) in which the traveling wave in the plasma is supposed to have a rather large amplitude. If the potential difference V_m between the top and the bottom of the wave amounts to almost a value given by

$$e V_m \approx (m/2)(v_b - v_w)^2, \quad (5.6)$$

where $v_w = \omega_0/k$ is the phase velocity of the wave, some electrons in the beam begin to be trapped in the potential valley. The number of trapped electrons would increase with the value of V_m . The maximum energy transferred to the wave per trapped electron is of the order of $m(v_b^2 - v_w^2)$. As the number of electrons incident on the plasma layer per unit time and per unit area is $n_b v_b$, the total rate of energy transferred from beam to wave is at most $n_b v_b (m/2)(v_b^2 - v_w^2)$. Hence, denoting the total energy of oscillation field as W , we may suppose $dW/dt \sim \text{constant}$ in such a limit; or W increases proportionally to time. In the linear theory we know that W builds up with a factor $\exp(2\gamma t)$. Thus the time increase of W is reduced to a linear rate from an exponential one.

In earlier discussions any loss of oscillations has not been taken into account. If

we consider various sorts of loss in the system, e.g., losses by collision, by reflection of wave at the layer-boundaries and the like, we might obtain $dW/dt \rightarrow 0$ which yields an oscillation with a stationary amplitude. Therefore it would be reasonable to regard the level given by (5.6) as the limit of large amplitude, since the magnitude of this level becomes for $\sigma^{1/3} \ll 1$

$$\frac{eV_m}{mv_b^2} \sim \left(1 - \frac{v_w}{v_b}\right)^2 \sim \sigma^{2/3}, \quad (5.7)$$

indicating that it coincides with the amplitude at which a strong bunching takes place.

§ 6. Case of Traveling Plasma Waves

Non-linear effects in the case of spatially growing plasma waves can also be discussed in quite a similar way as in the previous sections. For components of density modulation with a certain frequency and for their higher harmonics, we obtain the results as follows:

$$\frac{|n_{\omega^p}|}{n_p} = \frac{ek^2}{m\omega^2} V_{\omega}(0) e^{\gamma x} = r(x) \left(\frac{v_b}{v_w}\right)^2 \left(1 + \frac{\gamma^2}{k_0^2}\right), \quad (6.1)$$

$$\begin{aligned} \frac{|n_{\omega^b}|}{n_b} &= \frac{ek^2}{m|\omega - kv_b|^2} V_{\omega}(0) e^{\gamma x} \\ &= r(x) \left(\frac{v_b}{v_w}\right)^2 \frac{(1 + \gamma^2/k_0^2)}{|1 - kv_b/\omega|^2}, \end{aligned} \quad (6.2)$$

$$\frac{n_{2\omega}^p}{n_{\omega^p}^p} = -\frac{1}{2} \left(\frac{\omega^2}{\omega_p^2} I_2 + 3\right) \left(\frac{\omega_p}{\omega}\right)^4 \frac{n_{\omega^p}}{n_p} (1 + \sigma_{\omega})^2, \quad (6.3)$$

$$\begin{aligned} \frac{n_{2\omega}^b}{n_{\omega^b}^b} &= -\frac{1}{2} \left[\left(\frac{\omega - kv_b}{\omega_p}\right)^2 I_2 + 3 \right] \\ &\times \left(\frac{\omega_b}{\omega - kv_b}\right)^4 \frac{n_{\omega^b}}{n_b} \left(1 + \frac{1}{\sigma_{\omega}}\right)^2, \end{aligned} \quad (6.4)$$

where $k = k_0 - i\gamma$, $\sigma_{\omega} = n_{\omega^b}/n_{\omega^p}$. $V_{\omega}(0)$ is a modulation potential at the origin and

$$r(x) \equiv \frac{eV_{\omega}(0)e^{\gamma x}}{mv_b^2}. \quad (6.5)$$

If we estimate (6.1) to (6.4) for the case $\alpha^{1/3} \ll 1$ [see (A.12) and (A.13)], we get finally

$$\frac{|n_{\omega^p}|}{n_p} \sim r(x), \quad \frac{|n_{\omega^b}|}{n_b} \sim \frac{r(x)}{\alpha^{2/3}}, \quad (6.6)$$

$$\left|\frac{n_{2\omega}^b}{n_{\omega^p}^p}\right| \sim r(x), \quad \left|\frac{n_{2\omega}^b}{n_{\omega^b}^b}\right| \sim \frac{r(x)}{\alpha^{2/3}}, \quad (6.7)$$

and

$$\sigma_{\omega} = \left|\frac{n_{\omega^b}}{n_{\omega^p}}\right| \sim \frac{\sigma}{\alpha^{2/3}} \ll 1,$$

$$\sigma_{2\omega} = \left|\frac{n_{2\omega}^b}{n_{2\omega}^p}\right| \sim \frac{1}{\xi^2 \alpha^{1/3}} \text{ or } 1 \text{ according to } \xi^2 \alpha^{1/3} \gg 1 \text{ or } \leq 1.$$

Thus the criterion of validity of linear theory can be written as

$$r(x) \ll \alpha^{2/3}. \quad (6.8)$$

Then we can find

$$\begin{aligned} n_p &\gg |n_{\omega^p}| \gg |n_{2\omega}^p|, \\ n_b &\gg |n_{\omega^b}| \gg |n_{2\omega}^b|, \end{aligned} \quad (6.9)$$

If the wave propagates further, we get

$$r(x) \sim \alpha^{2/3}. \quad (6.10)$$

Then

$$\begin{aligned} n_p &\gg |n_{\omega^p}| \gg |n_{2\omega}^p|, \\ n_b &\sim |n_{\omega^b}| \sim |n_{2\omega}^b|, \end{aligned} \quad (6.11)$$

which shows a strong bunching of the beam and a small modulation in the plasma. As soon as the potential of the wave reaches about a value represented by (5.6), the running electrons are trapped in the potential trough. We can estimate such a magnitude of the potential with the aid of (A.12) and obtain

$$\frac{eV_m}{mv_b^2} \sim \alpha^{2/3}. \quad (6.12)$$

Comparing this with (6.10), we might conclude that the strong bunching and trapping of electrons in the beam would occur at the same level and the wave would saturate at the same time on account of some dissipation.

For the case of $\alpha^{1/3} \gg 1$, on the contrary, the electrons in the medium would be tightly bunched with much harmonics and the beam would be slightly modulated only by the fundamental component.

§ 7. Discussion

It is shown in §5 that the oscillating amplitude saturates when $r(t) \sim \sigma^{2/3}$ for $\sigma^{1/3} \ll 1$. Now we should like to see after how many cycles of oscillation the amplitude amounts to its ultimate level. For this we must estimate $r(t)$ of (4.16). Since $r(t)$ involves $V_k(0) = E_k(0)/ik$, $E_k(0)$ must be obtained. Here $E_k(0)$ is the mean amplitude of one mode in the thermal-plasma oscillations. Since the mean energy per mode is known as κT , we find

$$E_k(0) \sim (2\kappa T/\varepsilon_0)^{1/2} \sim 10^{-8} T^{1/2} \text{ volt/cm},$$

where T is measured by $^{\circ}\text{K}$ in the last expression.

For a numerical example, we take $\sigma \sim 1$, $T \sim 10^4 \text{ K}$, $mv_b^2 \sim 100 \text{ eV}$ and $k \sim 10$. Then from (4.16) and (5.1) we obtain $\exp(\gamma t) \ll 10^9$ and hence $\exp(\gamma t) \sim 10^8$ or $\gamma t \sim 18$. When $\sigma \sim 1$, $1/\gamma$ is about one period of oscillation. Thus we see the linear theory gives a reasonable results up to 20 cycles or so after the oscillation starts. After this time only a few cycles would be required for the saturation of amplitude.

If we suppose $\sigma \sim 10^{-3}$, with other parameters unaltered, we find the linear approximation is valid for $\exp(\gamma t) \ll 10^7$, namely for $\gamma t \sim 14$. In this case, however, $\gamma/\omega_0 \sim \sigma^{1/3} \sim 0.1$. Thus nearly a hundred cycles are allowable for the linear theory, and further twenty cycles are to be needed for the saturation.

Hitherto we have considered only a one-dimensional case. Therefore we have to take account of corrections due to the fact that the actual system is of three dimensions. If the electron beam has a finite cross section, the plasma wave excited would lose its energy through the surface of the beam as well as by reflection at both boundaries of the plasma layer. Furthermore the loss due to spectral decay would be possible by an additional non-linear effect.⁽¹¹⁾ If the total loss becomes comparatively large, the oscillation would be suppressed within the linear theory and if it is small enough, non-linear effects could be expected.

Finally the author is indebted to Professor T. Kihara of University of Tokyo and many members of our Laboratory for their interests and discussions.

Appendix

To make order-estimations of various quantities concerning a plasma wave excited with time, we shall first solve the dispersion relation

$$1 = \frac{\omega_p^2}{\omega^2} + \frac{\omega_b^2}{(\omega - kv_b)^2}, \quad (\text{A.1})$$

by approximating for $\sigma \ll 1$. Assume $\epsilon = (\gamma/\omega_0)^2 \ll 1$ and $\chi = (kv_b/\omega_0) - 1 \ll 1$. Then (A.1) is reduced to [see the reference 1)],

$$\left(\frac{\omega_0}{\omega_p}\right)^2 = 1 + \sigma \frac{\chi^2 - \epsilon}{(\chi^2 + \epsilon)^2}, \quad (\text{A.2})$$

$$(\chi^2 + \epsilon)^2 = \sigma \chi. \quad (\text{A.3})$$

The highest frequency is obtained for $\epsilon \rightarrow 0$, which results

$$\left(\frac{\omega_0}{\omega_p}\right)^2 = 1 + \chi \text{ and } \chi = \sigma^{1/3}.$$

Thus for $\sigma^{1/3} \ll 1$,

$$\left(\frac{\gamma}{\omega_p}\right)^2 = \epsilon \left(\frac{\omega_0}{\omega_p}\right)^2 \doteq \epsilon = \sqrt{\sigma \chi} - \chi^2. \quad (\text{A.4})$$

From this we get easily the maximum value of γ for $\chi = (\sigma/2)^{1/3}/2$. At this value we find

$$\begin{aligned} \frac{\omega_0}{\omega_p} &= 1 - \left(\frac{\sigma}{2}\right)^{1/3}, \quad \frac{\gamma}{\omega_p} = \frac{\sqrt{3}}{2} \left(\frac{\sigma}{2}\right)^{1/3}, \\ \frac{v_w}{v_b} &= 1 - \frac{1}{2} \left(\frac{\sigma}{2}\right)^{1/3}, \end{aligned} \quad (\text{A.5})$$

and

$$\frac{\omega_b}{|\omega - kv_b|} \sim \sigma^{1/6}, \quad \frac{kv_b}{|\omega|} \sim 1, \quad \frac{kv_b}{|\omega - kv_b|} \sim \sigma^{-1/3}. \quad (\text{A.6})$$

For $\sigma^{1/3} \gg 1$, according to the consideration given in section 5 of reference 1), we obtain

$$\frac{\omega_0}{\omega_b} = \frac{v_w}{v_b} = \frac{1}{2} \left(\frac{1}{2\sigma}\right)^{1/3}, \quad \frac{\gamma}{\omega_b} = \frac{\sqrt{3}}{2} \left(\frac{1}{2\sigma}\right)^{1/3}. \quad (\text{A.7})$$

Hence

$$\frac{\omega_b}{|\omega - kv_b|} \sim \frac{kv_b}{|\omega - kv_b|} \sim 1, \quad \frac{kv_b}{|\omega|} \sim \sigma^{1/3}, \quad \frac{|\omega|}{\omega_p} \sim \sigma^{1/6}. \quad (\text{A.8})$$

Now the integration I_2 is given by

$$I_2 = \left(\frac{\omega_p}{\omega}\right)^4 + \frac{\omega_p^2 \omega_b^2}{(\omega - kv_b)^4},$$

which becomes, according to $\sigma^{1/3} \ll 1$ and $\gg 1$,

$$I_2 \sim \sigma^{-1/3} \gg 1 \text{ and } I_2 \sim \sigma^{-2/3} \ll 1. \quad (\text{A.9})$$

In the case of traveling plasma wave, the assumptions $\chi = 1 - (\omega/kv_b) \ll 1$ and $\xi^2 = (v_b/v_T)^2 \gg 1$ give the approximate dispersion relation [see reference 3)],

$$\left(\frac{\omega}{\omega_p}\right)^2 = 1 + \frac{3}{2\xi^2} + \sigma \frac{(\chi^2 - \epsilon^2)}{(\chi^2 + \epsilon^2)^2}, \quad (\text{A.10})$$

$$(\chi^2 + \epsilon^2)^2 = \alpha \chi, \quad (\text{A.11})$$

where $\epsilon = \gamma/k_0$ and $\alpha = (2/3)\xi^2 \sigma$. For $\alpha^{1/3} \ll 1$, it is found γ attains its maximum for $\chi = (\alpha/2)^{1/3}/2$. Then we get

$$\frac{\omega}{\omega_p} = 1 + \frac{3}{4\xi^2}, \quad \frac{\gamma v_b}{\omega_p} = \frac{\sqrt{3}}{2} \left(\frac{\alpha}{2}\right)^{1/3},$$

$$\frac{v_w}{v_b} = 1 - \frac{1}{2} \left(\frac{\alpha}{2}\right)^{1/3},$$

and

$$\frac{\omega_b}{|\omega - kv_b|} \sim \frac{\sigma^{1/2}}{\alpha^{1/3}}. \quad (\text{A.12})$$

Thus I_2 becomes finally

$$I_2 \sim 1 + \frac{\sigma}{\alpha^{4/3}} \sim 1 + \frac{1}{\xi^2 \alpha^{1/3}}. \quad (\text{A.13})$$

References

- 1) M. Sumi: J. Phys. Soc. Japan **13** (1958) 1476.
- 2) M. Sumi: Phys. Rev. Letters **2** (1959) 37; J. Phys. Soc. Japan **14** (1959) 1093.
- 3) M. Sumi: J. Phys. Soc. Japan **14** (1959) 653.
- 4) M. Sumi: J. Phys. Soc. Japan **15** (1960) 120.
- 5) D. Bohm and E. P. Gross: Phys. Rev. **75** (1949) 1853.
- 6) S. F. Smerd: Nature **175** (1959) 297.
- 7) H. K. Sen: Phys. Rev. **97** (1955) 849.
- 8) A. I. Akhiezer and R. V. Polovin: Zh. Eks. Teor. Fiz. **30** (1956) 915.
- 9) R. V. Polovin: Zh. Eks. Teor. Fiz. **31** (1956) 354.
- 10) Ira B. Bernstein, J. M. Greene and M. D. Kruskal: Phys. Rev. **106** (1957) 546.
- 11) P. A. Sturrock: Proc. Roy. Soc. **242** (1957) 277.
- 12) L. Gold: J. Electronics **4** (1958) 219.
- 13) S. Amer: J. Electronics **5** (1958) 105.
- 14) J. M. Dawson: Phys. Rev. **113** (1959) 383.
- 15) Iu. L. Klimontovich: Zh. Eks. Teor. Fiz. **86** (1959) 1405; Sov. Phys. JETP. **36(9)** (1959) 999.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Oscillations in a Plasma in a Weak Magnetic Field

BY Kiyoe KATO

Tokyo University of Education, Otsuka, Tokyo

(Received February 19, 1960)

The oscillations in a bounded plasma in an external magnetic field were studied. The hot cathode discharge tubes used were filled with mercury vapour at pressure of the order of 10^{-3} mm Hg. The weak uniform magnetic field whose strength was in a region between 0 and 350 gauss was applied parallel to the direction of discharge current. The oscillations were detected by a super-regenerative detector adjusted to a constant frequency.

The oscillations of two types were detected: One has a frequency which depends on the magnetic field strength alone, and the other has a frequency which depends on the electron concentration as well as the magnetic field strength. The former is interpreted as the cyclotron resonance oscillation, and the latter as the plasma type oscillation.

§ 1. Introduction

The oscillations in a plasma generated in the discharge tubes of Merrill-Webb type¹⁾ have been investigated, and some of results were reported by Kojima et al. whose papers are hereafter referred to as **I**²⁾ and **II**³⁾. It was concluded there that the oscillations classified into three groups were observed in the discharge tube. In the present experiments, the oscillations in a plasma generated in the discharge tubes of the same type were investigated in the presence of the external magnetic field parallel to the direction of the discharge current. First, the changes of the

oscillations of three groups were observed in relation to the change of visual structure in the discharge tube, as the magnetic field strength was increased from zero. The results seem to support the interpretations given in **II**.

The frequency of the plasma oscillation observed in absence of an external magnetic field is nearly equal to the so-called plasma frequency given as

$$f_p = \sqrt{Ne^2/\pi m}, \quad (1)$$

where e and m are the charge and the mass of electron, respectively, and N is the elect-

ron concentration. When the plasma is put into an external magnetic field, the plasma type oscillation excited there should have a different frequency from f_p . Furthermore, it should be expected to give rise to the cyclotron resonance phenomena as the frequency of the plasma type oscillations closes to the cyclotron frequency or its multiples. The cyclotron frequency is represented by

$$f_c = eB/2\pi m \quad (2)$$

for the electron gyration in a magnetic field of strength B . On the other hand, the frequency of the plasma type oscillation excited in plasma in a magnetic field is given approximately by the well known expression

$$f = \sqrt{f_p^2 + f_c^2 \sin^2 \theta}, \quad (3)$$

where θ is the angle between the direction of propagation of oscillation and external magnetic field⁵⁾.

The plasma type oscillation in a magnetic field has been discussed theoretically by Gross⁴⁾ and Bernstein⁵⁾. It seems, however, that the plasma oscillations whose frequency is given by Eq. (3) have not yet been observed in any experiment. On the other hand, the theoretical treatments on the cyclotron resonance oscillations have been given by Hwa⁶⁾ and Kelly et al.⁷⁾. The experiments on the cyclotron resonance have been attempted in a rather strong magnetic field by Kelly et al.⁷⁾ and others⁸⁾. In the present experiments, the oscillations of two types mentioned above are detected in the weak magnetic field up to 350 gauss, and they are explained in correlation with each other. In the following, the procedures and the results of our experiments will be mentioned in detail, and the discussions on the results will be given.

§ 2. Experimental Apparatus and Procedure

The type of discharge tubes used is shown in Fig. 1. It is similar to that used in the previous experiments (II) on the plasma oscillations. They contained mercury drops, and hence they were filled with mercury vapour at a low pressure of the order of 10^{-8} mm Hg at the room temperature. The anode was a disk having a diameter of 12 mm, and was set 16 mm away from a cathode. The indirectly heated cathode was a cylinder, 5 mm in diameter and 10 mm deep, with an oxide-

coated front surface. A cathode made of nickel is preferable for an active emitting surface, but it disturbs the uniformity of magnetic field. Therefore, the electrodes made of platinum were also used. The two electrodes were injected into a glass sphere tube of 60 mm in diameter which was large enough to avoid the effect of tube wall on the plasma. A single tungsten wire probe, 0.1 mm in diameter and 2 mm long, could be moved through the region of the plasma, and picked up the oscillation.

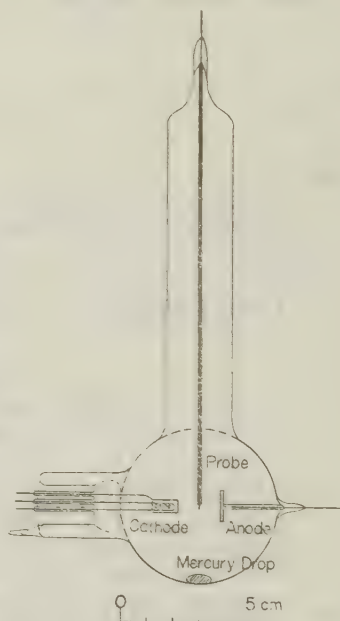


Fig. 1. Type of discharge tube.

A uniform magnetic field was furnished by a Helmholtz coil and was homogeneous within 1% over the plasma. The magnetic field strength was measured by a fluxmeter which was calibrated with a proton resonance. The magnetic field was applied parallel to the direction of discharge current, the strength of which was changed with a coil direct current in a region between 0 and 350 gauss. The coil current was modulated by use of a 50-c/s sine wave superimposed on a direct current.

Oscillations were detected by a super-regenerative detector capacitatively coupled to the movable probe, and after amplification the output was displayed on the vertical axis of an oscilloscope, the horizontal deflection of which was made proportional to the strength of the magnetic field. Thus the oscilloscope

displayed a plot of the intensity of the oscillation as a function of the strength of a magnetic field. The block diagram illustrating this experimental method is shown in Fig. 2.

Oscillations were observed by the detector adjusted to a constant frequency, because it was hard for our apparatus to change extensively the frequency of detector without giving considerable influence on its sensitivity.

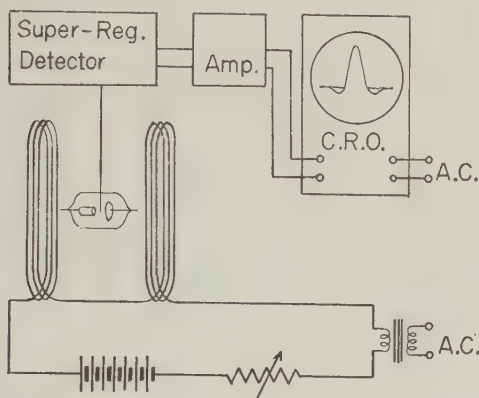


Fig. 2. Block diagram illustrating our experimental method.

As the magnetic field strength is increased, the frequency of oscillation in plasma would change, so that, in order to detect the oscillation by the detector with a fixed frequency, it is necessary to restore the frequency of oscillation by changing the discharge current. In the following section, most of results of measurements will be given in diagrams showing the relations of magnetic field strength to the discharge current which gives maximum amplitude to the detector. The following is ascertained in our experiments: If the discharge current is decreased as the magnetic field strength is increased, it implies that the frequency of oscillation would increase with the magnetic field strength if the discharge current were fixed. These circumstances correspond to the fact that the frequency of plasma type oscillation increases with the electron concentration or the discharge current. Hence, the qualitative changes of the frequency of oscillation due to the magnetic field strength can be conjectured from an experiment with a fixed frequency. The quantitative changes of the frequency due to the changes of the magnetic field strength or the discharge current were obtained

by doing the experiments with different fixed frequencies.

§3. Experimental Results and Discussions

(A). It was reported in II that the oscillations of three groups were detected in the tube mentioned above. These are the oscillations of the first group generated in the central part of plasma by a convergent beam, the oscillations of the second group generated in the wider region of the plasma by a divergent beam, and the oscillations of the third group generated at the periphery of the convergent beam. In order to verify these results still more, the changes of the behaviour of oscillations in plasma, as the magnetic field strength was increased from zero, were compared with the changes of visual structure of the plasma in tube. In this experiment the discharge tube with nickel electrodes was used. When the magnetic field was not applied, the convergent and the divergent beam and their boundary were clearly distinguished each other. This is shown schematically in Fig. 3. If the probe

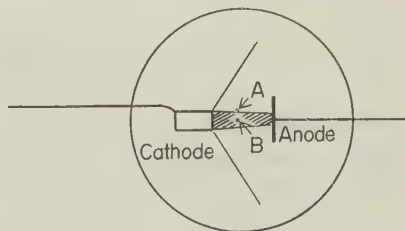


Fig. 3. Scheme demonstrating the visual structure of a plasma in the discharge tube.

is set at the position A in Fig. 3 where the convergent and divergent beams are clearly bounded, the oscillations of the third group alone can be detected. As the magnetic field strength was increased from 0, the behaviour of the oscillations having constant frequency $f_a = 720$ Mc, where f_a is frequency of the detector, changed as shown in Fig. 4. In (a) of Fig. 4, the external magnetic field strength H at which the oscillations of 720 Mc could be detected, is represented for the discharge current I_p , and in (b), the change of the intensity I_m of oscillations is shown. The relation of this behaviour to a visual structure in the tube is as follows: When the magnetic field strength was slightly increased from zero, the outside of convergent beam

got coloured brightly and the boundary of the convergent beam became less clear. In that case, the oscillations became unstable. At about 10 gauss, the contraction of plasma came in sight at the circumference, then the boundary of the convergent beam became clearer than before. Now, the oscillations became stable again and their intensity grew larger. Then the intensity arrived at maximum and the boundary of the beam kept clear for a while. After that, as the contrac-

tion at the circumference went on, the boundary of the beam became less and less clear. While, the oscillations weakened, and at about 25 gauss they disappeared. The above-mentioned supports the interpretation of the third group given in II.

The oscillations of the first and the second groups were inquired in the weak magnetic field up to 30 gauss. They were detected by a probe set at the central position *B* in the tube. Their behaviour is shown in Fig. 5. These plots represent a relation between the magnetic field strength and the discharge current: In this relation the oscillations of 755 Mc could be detected. From about 15 gauss, the oscillations of the second group weakened, and they disappeared above 20 gauss. The oscillations of the first group, considered as main plasma oscillations, once disappeared at about 30 gauss (This fact is also reported by M. D. Gabovich and L. L. Pasechnik⁹⁾) and appeared again at some larger magnetic field strength (~40 gauss). As to the behaviour of these oscillations, the experimental results and the discussions will be given in (B). In (B) the region of the stronger magnetic field is treated mainly, where the change of the visual structure is not observed.

(B). The observations of oscillations in a plasma in the axial external magnetic field,

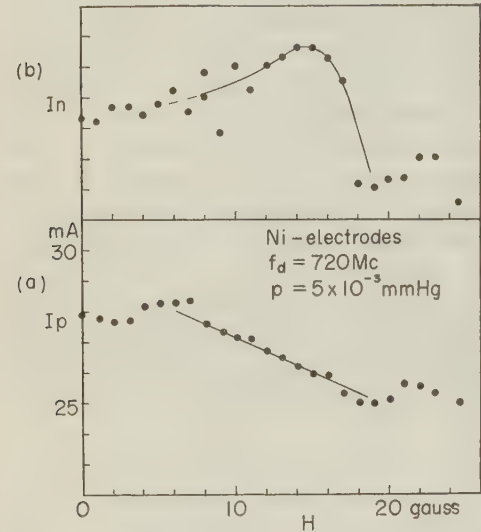


Fig. 4. (a) Plots of external magnetic field strength vs. discharge current, for the oscillation of the 3rd group. (b) Plots of its intensity vs. magnetic field strength.

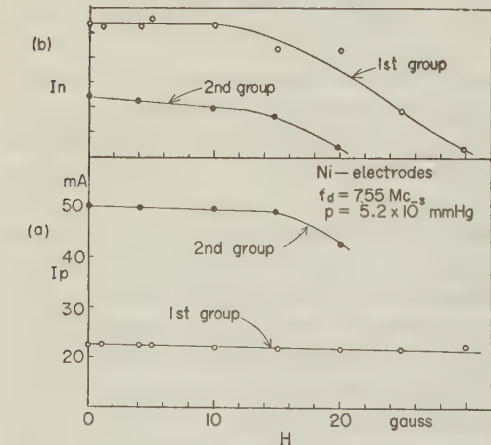


Fig. 5. (a) Plots of external magnetic field strength vs. discharge current, for the oscillations of the 1st and the 2nd group, respectively. (b) Plots of their intensity vs. magnetic field strength.

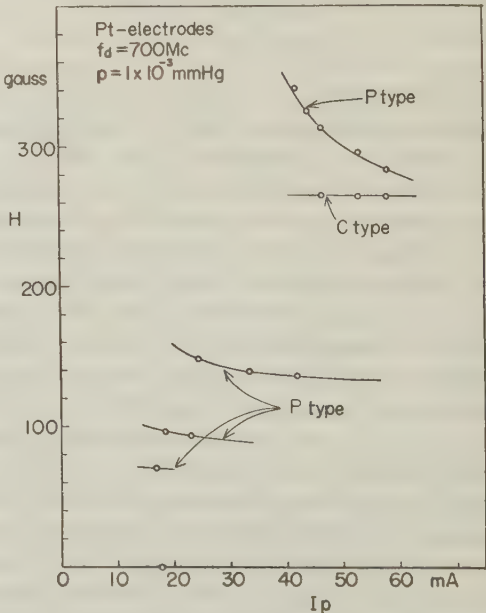


Fig. 6. H - I_p diagram for the oscillations observed by the detector adjusted at 700 Mc.

whose strength was changed from 0 to 350 gauss, were carried out by using the tube with platinum electrodes. First, oscillations were detected through a probe by a super-regenerative detector adjusted to 700 Mc. Since the observed oscillations were considerably broad, the field strength giving the maximum intensity was plotted against the discharge current. A $H-I_p$ diagram obtained by such a way is shown in Fig. 6, which represents a relation between the external magnetic field H and the discharge current I_p . In this relation the oscillations of constant frequencies were detected. It is found from this result that the oscillations of two types were detected: These are the oscillation distinguished as C type, whose frequency depends on the magnetic field alone, but not on the discharge current, and the oscillation distinguished as P type, whose frequency changes with discharge current or electron concentration. Therefore the oscillation of C type is possibly interpreted as the cyclotron resonance oscillation having the frequency given by Eq. (2). On the other

hand, as shown in the following, it is possible to explain the oscillation of P type as the plasma type oscillation having the frequency given approximately by Eq. (3).

1. *Plasma oscillation.* According to Bernstein,⁵⁾ the dispersion relation for the plasma waves of angular frequency ω is given, in the presence of magnetic field, by

$$\omega^2 \simeq \omega_p^2 + \omega_o^2 \sin^2 \theta + 3(\kappa T/m)k^2, \quad (4)$$

where $\omega_p = 2\pi f_p$, $\omega_o = 2\pi f_c$, κ and T are the Boltzmann constant and electron temperature, respectively, and k is the wave number. In the limiting case $T \rightarrow 0$, Eq. (4) is reduced to Eq. (3), and the frequency of the oscillations excited in plasma is determined by the electron concentration and the magnetic field strength. In our case, the temperature of plasma electron is low enough ($\sim 10^4$ K) and k is the order of $1 \sim 10 \text{ cm}^{-1}$, so that the Eq. (3) is applicable. Furthermore, it is known that for oscillations propagating perpendicular to the external magnetic field, there are gaps in the spectrum of allowed frequencies at multiples of the electron gyration frequency.^{4), 5)} This existence of gaps may be explained as

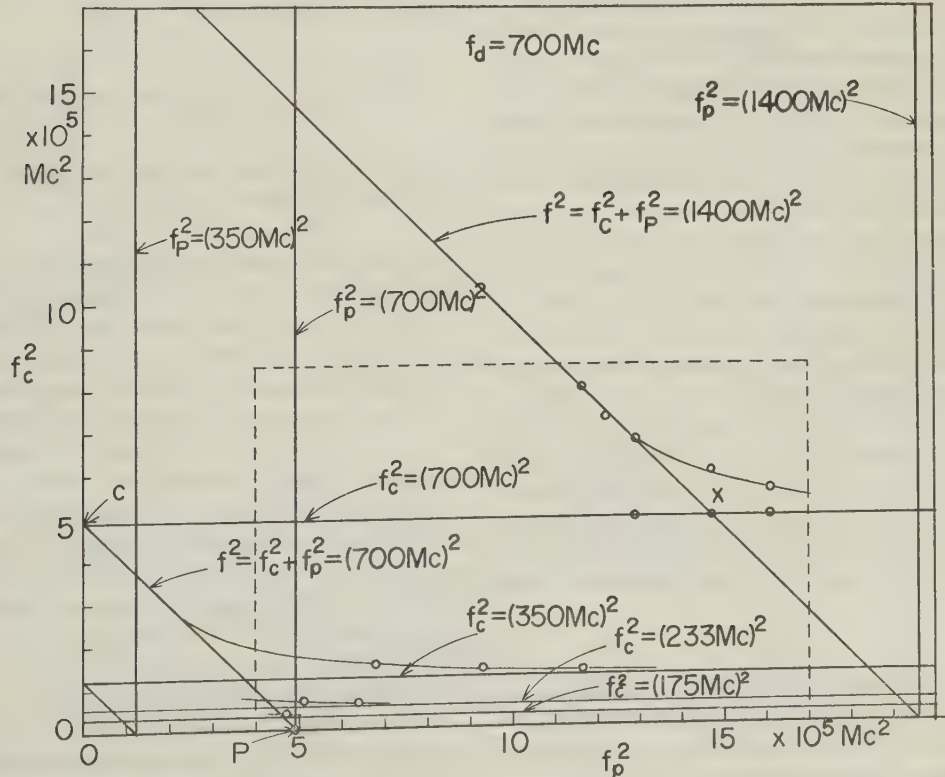


Fig. 7. f_c^2 - f_p^2 diagram transformed from H - I_p diagram in Fig. 6.

a sort of resonance phenomena taking place at $\omega = n\omega_c$.

In a diagram which takes f_p^2 as an abscissa and f_c^2 as an ordinate, the expressions $f^2 = f_p^2 + f_c^2 = \text{const.}$ and $f^2 = f_p^2$ are represented by straight lines. The observed plots should be in the region between these two straight lines if the direction of propagation of wave is taken into account. f_c is proportional to H , and f_p^2 is considered to be proportional to I_p similarly to the case of no magnetic field in **I**, so far as the visual structure in tube does not change and the contraction is not observed. Therefore the plots in $H-I_p$ diagram are transformed easily to the $f_c^2-f_p^2$ diagram. (For example, $I_p = 18 \text{ mA}$ for $f_p = 700 \text{ Mc}$. When the contraction of plasma in weak magnetic field was remarkable, the relation of I_p to f_p was obtained by finding the change of I_p due to the contraction as the magnetic field strength was increased from zero to a small value for which f_c is small compared with f_p , and by extrapolating this change to a field strength for which the contraction could not be seen.) In Fig. 7, the line $f^2 = (700 \text{ Mc})^2$ is drawn through the two points *C* and *P*, where *C* is corresponding to the oscillation of *C* type detected at 700 Mc, and *P* is corresponding to the plasma oscillation in the absence of magnetic field. The experimental plots were transformed from $H-I_p$ diagram to $f_c^2-f_p^2$ diagram in Fig. 7. The region enclosed with dotted line is the observable region by our apparatus. It is remarkable that the plots are placed in the neighbourhood of lines $f^2 = (2f_a)^2$ and $f_c^2 = f_a^2$, where $f_a = 700 \text{ Mc}$. (See also Fig. 9 and 10.) From these diagrams, it is clear that the oscillations having the frequencies 700 Mc, 1400 Mc and others (350 Mc, etc.) were detected simultaneously by our detector adjusted to 700 Mc. Accordingly, it is reasonable to consider that the oscillations of *P* type are mainly the plasma type oscillations propagating perpendicular to the external magnetic field and having the frequency f approximately given by

$$f = \sqrt{f_p^2 + f_c^2}. \quad (5)$$

Since the plasma oscillation is excited by a beam gyrating in a magnetic field, it may be considered that the oscillation propagates in a direction perpendicular to the field.

Furthermore, the experimental plots had a

tendency to shift towards the large value of $-f_p^2$ in $f_c^2-f_p^2$ diagram, as $2f_c$ closes to f with change of the magnetic field strength. In other words, the observed frequencies become smaller than the value given by expression (5). After that, the oscillations of *P* type are quenched discontinuously in the neighbourhood of $f = 2f_c$ (i. e., in the neighbourhood of *X* in Fig. 7 for the plasma type oscillation of frequency 1400 Mc). These facts may be considered in connection with the resonance phenomena. It seems that as the results of enhancement of organized electron gyration at the neighbourhood of $f = 2f_c$, the state of plasma is considerably changed, so that the approximation used in reduction of Eq. (5) becomes unacceptable. Furthermore, owing to the large energy transfer to the cyclotron oscillation of frequency f_c , the maintenance of the plasma type oscillation of frequency nf_c may be forbidden.

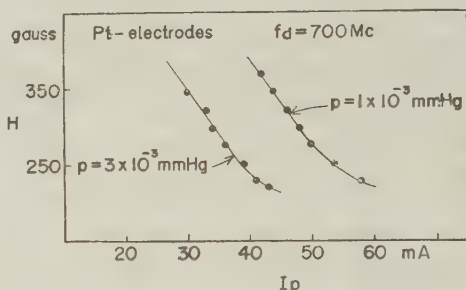


Fig. 8. $H-I_p$ diagram for the oscillations observed at the different pressures.

In the experiments reported above, the temperature of the tube, and hence the pressure in the tube were kept constant through the observation. When the oscillations were observed in plasma in different pressures, the $H-I_p$ diagrams were obtained as shown in Fig. 8. In these cases the detector was also adjusted to the frequency of 700 Mc. It is found that the plots corresponding to the plasma type oscillations of constant frequency shift towards the small value of I_p in $H-I_p$ diagram, as the pressure becomes larger.

The intensity of oscillation of *P* type was several times larger than that of *C* type when they were observed simultaneously.

2. *Cyclotron resonance oscillation.* The oscillations of *C* type considered to be the cyclotron resonance oscillations were detected with three different frequencies of detector

together with the oscillations of plasma type with twofold frequencies. These are given in Fig. 9 by $H-I_p$ diagram. These plots

were transformed to the $f_o^2-f_p^2$ diagram, as shown in Fig. 10. It seems that this diagram gives some support to the above explanation on the oscillation of P type. The oscillation of C type has a tendency that their intensity becomes larger as the discharge current increases and f closes to $2f_o$.

Combining with the experimental plots of different frequencies one another, we can draw the frequency characteristics for the applied magnetic field strength as shown in Fig. 11. This diagram tells us that the frequencies of oscillations of C type are somewhat smaller systematically than the calculated cyclotron frequency from the external magnetic field strength. These differences are the order of several percent for the magnitude of f_o . If these discrepancies are attributed to the diamagnetism of plasma entirely, they are considerably larger than expected value from the theoretical point of view. However, when the experiments were performed using the nickel electrodes instead of the platinum, the above difference was hardly shown. Accordingly the difference between

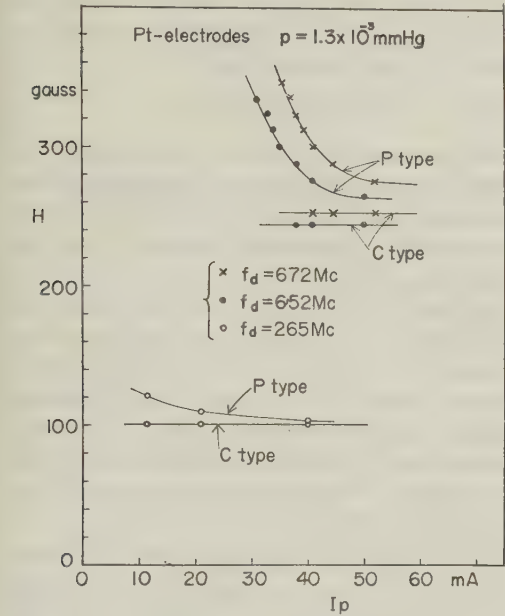


Fig. 9. $H-I_p$ diagram for the oscillations observed with different frequencies of detector.

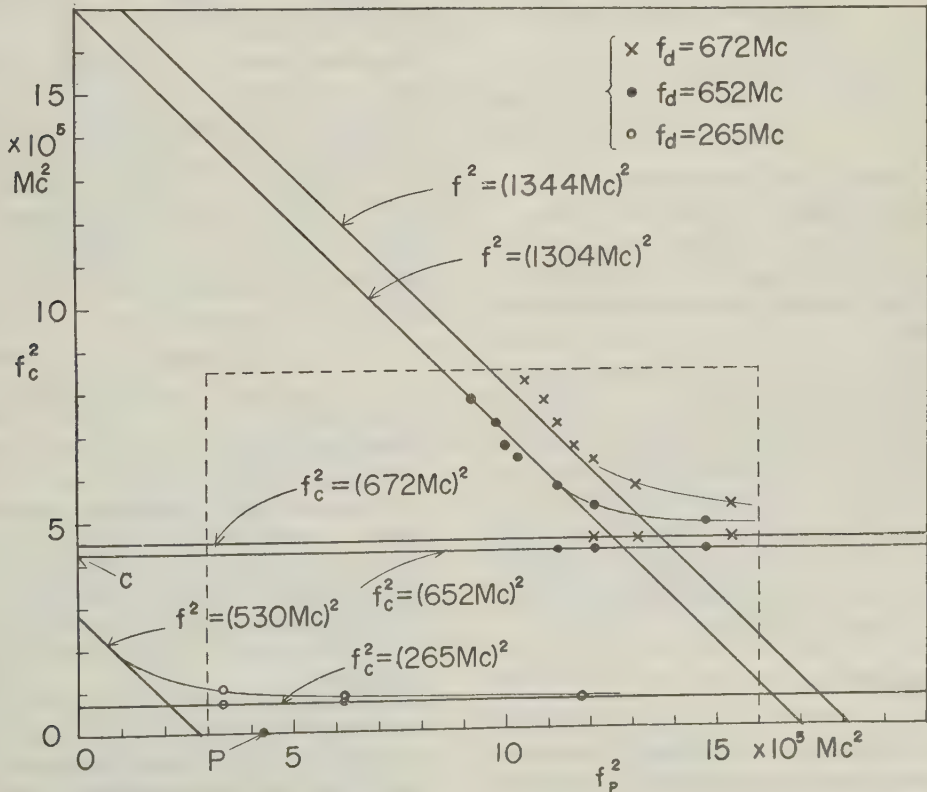


Fig. 10. $f_o^2-f_p^2$ diagram transformed from $H-I_p$ diagram in Fig. 9.

external and internal magnetic field strength may be considered to be the order of magnitude which is able to cancel out the magnetic field induced by the nickel electrodes. While, by Max Steenbeck,¹⁰⁾ it was shown experimentally that the plasma in magnetic field exhibits the large diamagnetism of the order of 0.1~1% which is larger than his theoretical value. It is also possible to give another explanation based on the concept of effective mass of electron which follows from the disturbance for electron gyration by ion. But in our case of low pressure, the effect of the electron effective mass is small that it may be neglected.

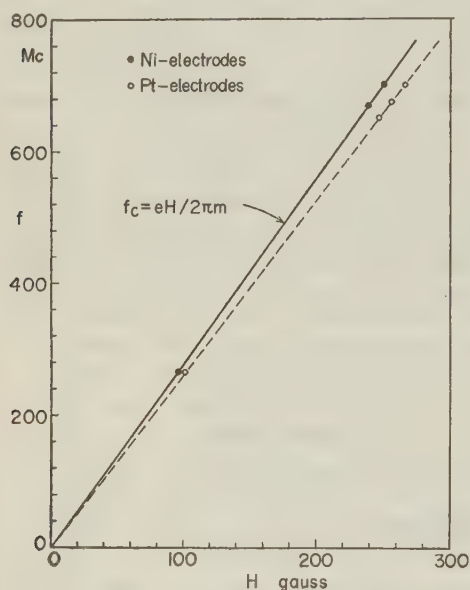


Fig. 11. Observed frequencies of cyclotron oscillations for the applied external magnetic field strength.

The half width was measured for the cyclotron resonance oscillation. It is, for example, about 15 Mc at resonance frequency of 700 Mc. Namely, the ratio of the half width to cyclotron frequency is about 0.02 for the electron concentration of about 10^{10} cm^{-3} , and it is consistent with the value given by Hwa.⁶⁾ Then the collision time is calculated from it to be the order of 10^{-8} sec .

§ 4. Conclusion

In the presence of an external magnetic field, the oscillation of two types are observed in the plasma generated in a discharge tube. These are interpreted as the plasma

type oscillations and as the cyclotron oscillations, respectively. The former is the oscillation excited by a convergent beam at the central region of the tube, and is corresponding to that of the first group in II. Its frequency is given approximately by

$$f = \sqrt{f_p^2 + f_c^2},$$

but as it closes to the twofold cyclotron frequency it becomes smaller than the above expression, and after that, it is quenched discontinuously. These results seem to be consistent with the theory given up to this time.

The oscillation generated in the wider region of plasma by a divergent electron beam disappeared as the plasma is contracted by a magnetic field. The intensity of the oscillation generated at a clear boundary of a main electron beam is increased with clarity of the boundary. These results support the interpretation given in II.

The frequency of the observed cyclotron resonance oscillation is somewhat smaller than the calculated cyclotron frequency from the external magnetic field strength. If these discrepancies attributed entirely to the diamagnetism of plasma, it is far larger than the theoretical value.

The author wishes to express her sincere thanks to Professor S. Kojima for his guidance and encouragement. The author is also indebted to Dr. K. Takayama and Dr. M. Sumi of the Electrical Communication Laboratory for their interest and valuable discussions, and to Dr. S. Hagiwara, Dr. S. Ohara and Mr. R. Matsuzaki for help on experiments.

References

- 1) H. J. Merrill and H. W. Webb: *Phys. Rev.* **55** (1939) 1191.
- 2) S. Kojima, K. Kato and S. Hagiwara: *J. Phys. Soc. Japan* **12** (1957) 1276.
- 3) S. Kojima, K. Kato, S. Hagiwara and R. Matsuzaki: *J. Phys. Soc. Japan* **14** (1959) 821.
- 4) E. P. Gross: *Phys. Rev.* **82** (1951) 232.
- 5) I. B. Bernstein: *Phys. Rev.* **109** (1958) 10.
- 6) R. C. Hwa: *Phys. Rev.* **110** (1958) 307.
- 7) D. C. Kelly and S. C. Brown: *Phys. Rev.* **108** (1957) 1367.
- 8) D. J. E. Ingram and J. G. Tapley: *Phys. Rev.* **97** (1955) 238. K. Fukuda, H. Matsumoto, Y. Uchida and H. Yoshimura: *J. Phys. Soc. Japan* **14** (1959) 543. R. M. Hill and S. J. Tetenbaum: *J. Appl. Phys.* **30** (1959) 1610.

- 9) M. D. Gabovich and L. L. Pasechnik: J. Exp. Theor. Phys. (U. S. S. R.) **36** (1959) 1025. 10) M. Steenbeck: Wiss. Veroff. Siemens-Konz. **15** (2)(1936) 1.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 15, No. 6, JUNE, 1960

Transport Properties of Plasmas in a Strong Magnetic Field

By Taro KIHARA, Yukio MIDZUNO, and Shobu KANEKO

*Department of Physics, Faculty of Science,
University of Tokyo*

(Received March 5, 1960)

Irreversible processes in plasmas in a strong magnetic field are discussed from both phenomenological and microscopic points of view. The thermodynamics of irreversible processes is applied and it is shown that the Onsager-Casimir reciprocity relation takes a symmetrical form for plasmas in a magnetic field. For a two-component fully ionized gas where the electrons make many free gyrations interference between electrical and thermal conductions vanish. When the mean gyration radius r_g of the electrons is shorter than the Debye length l_D , the diagonal elements of tensors of the electric conductivity and diffusion coefficient perpendicular to the magnetic field are proportional to

$$\ln(kTl_D/Ze^2) + (3/4)[\ln(l_D/r_g)]^2,$$

where Ze and $-e$ are the charges of an ion and electron respectively.

§ 1. Introduction

Theory of irreversible processes may be divided into phenomenological (or macroscopic) approach and molecular (or microscopic) approach. The purpose of the phenomenological theory in this paper is an application of the thermodynamics of irreversible processes to plasmas in a strong magnetic field; and the main purpose of our microscopic theory is an application of the force-correlation formalism to a gaseous plasma.

In the absence of the magnetic field, or for weak fields at most, the phenomenological coefficients in linear relations for irreversible processes are scalars. This case has been treated by Maecker and Peters¹⁾ and by Kihara²⁾. In the presence of a strong magnetic field these coefficients are tensors, whose characteristic features will be discussed in this paper.

When the mean gyration radius of electrons is larger than the Debye length, the microscopic theory can be developed by use of the Boltzmann equation; in fact many works have been done along this line³⁾⁴⁾⁵⁾⁶⁾. In the pres-

ent paper the electron gyration radius can be smaller than the Debye length, and the Boltzmann equation will not be used.

§ 2. Phenomenological Foundation

The thermodynamics of irreversible processes, which has been developed since Onsager-Casimir's reciprocity theorem, will be applied, in Section 2 and 3, to plasmas in a strong magnetic field. A fundamental assumption is that the system is not far from thermal equilibrium. We shall consider plasmas composed of several species of component fluids in which neither ionization nor recombination occurs and radiation plays no role. We suppose that no temperature difference exists between plasma components and that the viscosity is negligible.

Let n_j and v_j be, respectively, the number density and the flow velocity of j th component. Then equation of continuity for the component is

$$\partial n_j / \partial t + \operatorname{div}(n_j v_j) = 0. \quad (2.1)$$

Denoting by $n_j m_j$ and $n_j e_j$ the mass and charge densities of the j th component, we

adopt the equation of motion

$$\begin{aligned} \sum n_j m_j \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \text{grad} \right) \mathbf{v} \\ = \sum n_j \left[e_j \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_j \times \mathbf{B} \right) + m_j \mathbf{g} \right] - \text{grad } P \end{aligned}$$

for the plasma as a whole. Here $\mathbf{v}$ is the average flow

$$\mathbf{v} = \sum n_j m_j \mathbf{v}_j / \sum n_j m_j \quad (\Sigma \equiv \sum_j),$$

$\mathbf{E}$ and $\mathbf{B}$ the electric and the magnetic fields, $\mathbf{g}$ the gravitational acceleration, and P the pressure. (The Gauss system of units is used, and $c = 3 \times 10^{10}$ cm/sec.) The equation of motion can be written in the form

$$\sum n_j \mathbf{F}_j^* - \text{grad } P = 0, \quad (2.2)$$

where

$$\begin{aligned} \mathbf{F}_j^* = e_j \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_j \times \mathbf{B} \right) \\ + m_j \left[\mathbf{g} - \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \text{grad} \right) \mathbf{v} \right]. \end{aligned} \quad (2.3)$$

Following Prigogine⁷⁾ we "decompose" the pressure gradient into

$$\text{grad } P = \sum n_j (\text{grad } \mu_j)_T.$$

Here μ_j is the chemical potential per particle of the j th species and

$$(\text{grad } \mu_j)_T \equiv \text{grad } \mu_j - \left(\frac{\partial \mu_j}{\partial T} \right)_{P, \text{composition}} \text{grad } T,$$

T being the temperature. The equation of motion (2.2) then becomes

$$\sum n_j [\mathbf{F}_j^* - (\text{grad } \mu_j)_T] = 0. \quad (2.4)$$

Assuming that the plasma is not very far from thermal equilibrium, we can adopt the thermodynamics of irreversible processes, which gives the rate of entropy production $(\partial s / \partial t)_{\text{irr}}$ due to irreversible processes in the form²⁾

$$\begin{aligned} T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} = - \mathbf{q} \cdot \text{grad } \ln T \\ + \sum n_j \mathbf{v}_j \cdot [\mathbf{F}_j^* - (\text{grad } \mu_j)_T]. \end{aligned} \quad (2.5)$$

Here $\mathbf{q}$ is the heat flow, sometimes called reduced heat flow, due to conduction.

By virtue of (2.4), $\mathbf{v}_j$ and $\mathbf{F}_j^*$ in (2.5) can be replaced respectively by $\mathbf{v}_j - \mathbf{v}$ and

$$\begin{aligned} \mathbf{F}_j \equiv e_j \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \\ + m_j \left[\mathbf{g} - \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \text{grad} \right) \mathbf{v} \right], \end{aligned} \quad (2.6)$$

namely

$$\begin{aligned} T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} = - \mathbf{q} \cdot \text{grad } \ln T \\ + \sum n_j (\mathbf{v}_j - \mathbf{v}) \cdot [\mathbf{F}_j - (\text{grad } \mu_j)_T]. \end{aligned} \quad (2.7)$$

The entropy production (2.5) or (2.7) indicates that forces conjugate to fluxes $\mathbf{q}$ and $\mathbf{v}_j$ are respectively

$$-\text{grad } \ln T \text{ and } n_j [\mathbf{F}_j^* - (\text{grad } \mu_j)_T].$$

With forces $\mathbf{X}_\alpha$ conjugate to fluxes $\mathbf{Y}_\alpha$ the entropy production (2.5) or (2.7) is thus expressed in the form

$$T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} = \sum_\alpha \mathbf{X}_\alpha \cdot \mathbf{Y}_\alpha. \quad (2.8)$$

When a linear relation

$$\mathbf{X}_\alpha = \sum L_{\alpha\beta} \mathbf{Y}_\beta \quad (2.9)$$

is assumed among forces and fluxes, the so-called phenomenological coefficients $L_{\alpha\beta}$ are tensors. For the choice (2.9) of the linear relation the Onsager-Casimir reciprocity⁸⁾ takes the simplest form

$$L_{\alpha\beta}(\mathbf{B}) = L_{\beta\alpha}^\dagger(-\mathbf{B}). \quad (2.10)$$

This relation means that the tensor $L_{\alpha\beta}$ in the magnetic field $\mathbf{B}$ is equal to the transposed tensor $L_{\beta\alpha}^\dagger$ in the field $-\mathbf{B}$.

Let us take in the plasma a rectangular coordinate system with the z -axis in the direction of $\mathbf{B}$. Then each tensor is of the form

$$L_{\alpha\beta} = \begin{pmatrix} L_{\alpha\beta}^I & -L_{\alpha\beta}^{II} & 0 \\ L_{\alpha\beta}^{II} & L_{\alpha\beta}^I & 0 \\ 0 & 0 & L_{\alpha\beta}^{III} \end{pmatrix} \quad (2.11)$$

because the tensor must be invariant with respect to rotations about the z -axis. Furthermore (2.11) must be invariant with respect to the transformation

$$\mathbf{B} \rightarrow -\mathbf{B}, \quad z \rightarrow -z, \quad y \rightarrow -y,$$

hence

$$\begin{aligned} L_{\alpha\beta}^I(\mathbf{B}) &= L_{\alpha\beta}^I(-\mathbf{B}), \\ L_{\alpha\beta}^{II}(\mathbf{B}) &= -L_{\alpha\beta}^{II}(-\mathbf{B}), \\ L_{\alpha\beta}^{III}(\mathbf{B}) &= L_{\alpha\beta}^{III}(-\mathbf{B}) \end{aligned}$$

or

$$L_{\alpha\beta}(\mathbf{B}) = L_{\alpha\beta}^\dagger(-\mathbf{B}). \quad (2.12)$$

From (2.10) and (2.12) we obtain therefore

$$L_{\alpha\beta}(\mathbf{B}) = L_{\beta\alpha}(\mathbf{B}) \quad (2.13)$$

for all α and β .

In a weak magnetic field the phenomenological coefficients $L_{\alpha\beta}$ are scalars independent of the magnetic field for which the Onsager-Casimir reciprocity is simply $L_{\alpha\beta} = L_{\beta\alpha}$. This

case has been treated by Maecker and Peters¹¹. It is a characteristic feature of (otherwise isotropic) plasmas in a magnetic field that the Onsager-Casimir reciprocity (2.10) reduces to the simple reciprocal relation (2.13) between tensors.

If, instead of (2.9), we express the linear relation in such a "mixed" form as

$$\begin{aligned} Y_0 &= K_{00}X_0 + \sum_i K_{0i}Y_i \\ X_j &= K_{j0}X_0 + \sum_i K_{ji}Y_i \quad (j=1, 2, \dots) \end{aligned} \quad (2.14)$$

then the reciprocity relation becomes

$$K_{0j} = -K_{j0}, \quad K_{ji} = K_{ij}. \quad (2.15)$$

§ 3. Linear Relations

(a) Equation of motion for components

From (2.5), follows the linear relation

$$\begin{aligned} \mathbf{q} &= -K_{00}\text{grad} \ln T + \sum_i K_{0i}\mathbf{v}_i, \\ n_j[\mathbf{F}_j^* - (\text{grad } \mu_j)_T] &= -K_{j0}\text{grad} \ln T + \sum_i K_{ji}\mathbf{v}_i, \end{aligned} \quad (3.1)$$

of the type (2.14) with coefficient tensors satisfying the reciprocity (2.15). As the entropy production is always positive, the quadratic form for the coefficients is positive definite; in particular, tensors K_{00} and K_{jj} are positive, the thermal conductivity $\lambda \equiv K_{00}/T$ being positive. By virtue of (2.4) hold the relations

$$\sum_j K_{j0} = \sum_j K_{0j} = 0, \quad \sum_j K_{ji} = \sum_j K_{ij} = 0. \quad (3.2)$$

The second set of equations (3.1) gives the equation of motion of each component which can be transformed, by use of (3.2), into

$$\begin{aligned} n_j[\mathbf{F}_j^* - (\text{grad } \mu_j)_T] + K_{j0}\text{grad} \ln T \\ + \sum_i (-K_{ji})(\mathbf{v}_i - \mathbf{v}_j) = 0. \end{aligned} \quad (3.3)$$

The term with K_{j0} indicates as inner force due to thermal diffusion and the last term is the friction due to relative motion. For two-component plasmas the coefficient of friction $-K_{12}$ is positive definite.

(b) Transport coefficients

In the following we neglect the gravitation and inertia,

$$\mathbf{g} - \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \text{grad} \right) \mathbf{v} = 0.$$

Then (2.7) becomes

$$\begin{aligned} T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} &= -\mathbf{q} \cdot \text{grad} \ln T + \sum n_j(\mathbf{v}_j - \mathbf{v}) \\ &\cdot \left[e_j \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) - (\text{grad } \mu_j)_T \right]. \end{aligned} \quad (3.4)$$

In the absence of the mutual diffusion, i.e. when

$$\sum n_j(\mathbf{v}_j - \mathbf{v}) \cdot (\text{grad } \mu_j)_T = 0,$$

(3.4) reduces to

$$T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} = -\mathbf{q} \cdot \text{grad} \ln T + \mathbf{J} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \quad (3.5)$$

in terms of the conduction current

$$\mathbf{J} = \sum n_j e_j (\mathbf{v}_j - \mathbf{v}). \quad (3.6)$$

From (3.5) follows the linear relation

$$\left. \begin{aligned} \mathbf{q} &= -T\lambda \text{grad} \ln T + \alpha \mathbf{J} \\ \mathbf{E} + c^{-1} \mathbf{v} \times \mathbf{B} &= \alpha \text{grad} \ln T + \eta \mathbf{J} \end{aligned} \right\} \quad (3.7)$$

λ, η, α being tensors of the type (2.11):

$$\lambda = \begin{pmatrix} \lambda^I & -\lambda^{II} & 0 \\ \lambda^{II} & \lambda^I & 0 \\ 0 & 0 & \lambda^{III} \end{pmatrix}, \text{ etc.}$$

The λ is the thermal conductivity and η is the electric resistivity, both being positive definite.

Returning to (3.4) we next consider a neutral two-component plasma under uniform pressure

$$n_1 e_1 + n_2 e_2 = 0,$$

$$n_1 (\text{grad } \mu_1)_T + n_2 (\text{grad } \mu_2)_T = 0.$$

Then it follows that

$$\begin{aligned} e_1^{-1} (\text{grad } \mu_1)_T &= e_2^{-1} (\text{grad } \mu_2)_T \\ &= (e_1 - e_2)^{-1} [(\text{grad } \mu_1)_T - (\text{grad } \mu_2)_T] \end{aligned}$$

Then (3.4) can be transformed into

$$\begin{aligned} T \left(\frac{\partial s}{\partial t} \right)_{\text{irr}} &= -\mathbf{q} \cdot \text{grad} \ln T \\ &+ \mathbf{J} \cdot \{ \mathbf{E} + c^{-1} \mathbf{v} \times \mathbf{B} - (e_1 - e_2)^{-1} \\ &\times [(\text{grad } \mu_1)_T - (\text{grad } \mu_2)_T] \}, \end{aligned}$$

the corresponding linear relation being

$$\left. \begin{aligned} \mathbf{q} &= -T\lambda \text{grad} \ln T + \alpha \mathbf{J}, \\ \mathbf{E} + c^{-1} \mathbf{v} \times \mathbf{B} &= (e_1 - e_2)^{-1} [(\text{grad } \mu_1)_T - (\text{grad } \mu_2)_T] \\ &= \alpha \text{grad} \ln T + \eta \mathbf{J}. \end{aligned} \right\} \quad (3.9)$$

Here we introduce the electric conductivity σ , which is the inverse η^{-1} to the electric resistivity, or

$$\begin{aligned} \sigma^I &= \frac{\eta^I}{(\eta^I)^2 + (\eta^{II})^2}, & \sigma^{II} &= \frac{-\eta^{II}}{(\eta^I)^2 + (\eta^{II})^2}, \\ \sigma^{III} &= \frac{1}{\eta^{III}} \end{aligned} \quad (3.10)$$

in terms of the components

$$\eta = \begin{pmatrix} \eta^I & -\eta^{II} & 0 \\ \eta^{II} & \eta^I & 0 \\ 0 & 0 & \eta^{III} \end{pmatrix}, \quad \sigma = \begin{pmatrix} \sigma^I & -\sigma^{II} & 0 \\ \sigma^{II} & \sigma^I & 0 \\ 0 & 0 & \sigma^{III} \end{pmatrix}$$

concerning the rectangular coordinate system with the z -axis in the direction of $\mathbf{B}$. Then we have, for $\mathbf{E} + c^{-1}\mathbf{v} \times \mathbf{B} = 0$, the equation of diffusion

$$\begin{aligned} \mathbf{v}_1 - \mathbf{v}_2 &= \mathbf{J}/n_1 e_1 \\ &= -\sigma(n_1 e_1^2 + n_2 e_2^2)^{-1} [(\text{grad } \mu_1)_T - (\text{grad } \mu_2)_T] \\ &\quad - \sigma \alpha (n_1 e_1)^{-1} \text{grad } \ln T. \end{aligned}$$

Introducing the "modified" diffusion coefficient D^* and the thermal diffusion ratio k_T by

$$\begin{aligned} \mathbf{v}_1 - \mathbf{v}_2 &= -D^* \left\{ \frac{1}{kT} [(\text{grad } \mu_1)_T - (\text{grad } \mu_2)_T] \right. \\ &\quad \left. + \frac{(n_1 + n_2)^2}{n_1 n_2} k_T \text{grad } \ln T \right\} \end{aligned} \quad (3.11)$$

with the Boltzmann constant k , we obtain finally

$$D^*/kT = \sigma / (n_1 e_1^2 + n_2 e_2^2), \quad (3.12)$$

$$\frac{(n_1 + n_2)^2}{n_1 n_2} k_T = \frac{n_1 e_1^2 + n_2 e_2^2}{n_1 e_1} \frac{\alpha}{kT}. \quad (3.13)$$

In the following we consider a dilute gaseous plasma for which the chemical potential μ_j of j th species is related to the partial pressure P_j of the same species simply by

$$n_j (\text{grad } \mu_j)_T = \text{grad } P_j.$$

The modified diffusion coefficient D^* then reduces to the conventional diffusion coefficient

$$D = \begin{pmatrix} D^I & -D^{II} & 0 \\ D^{II} & D^I & 0 \\ 0 & 0 & D^{III} \end{pmatrix}$$

defined by

$$\mathbf{v}_1 - \mathbf{v}_2 = -D(n_1^{-1} \text{grad } n_1 - n_2^{-1} \text{grad } n_2), \quad (3.14)$$

and (3.12) reduces to the Einstein type relation

$$D/kT = \sigma / (n_1 e_1^2 + n_2 e_2^2). \quad (3.15)$$

§ 4. Diffusion and Electric Conduction

In this and the following sections transport coefficients across a strong magnetic field will be calculated, forces and fluxes being supposed to be perpendicular to the magnetic field. We consider a fully ionized gas composed of one type of positive ion, as species 1, and electrons, as species 2. The electric charge of an ion will be denoted by $e_1 = Ze$ and that of an electron by $e_2 = -e$; charge

neutrality $Zn_1 = n_2$ (or quasi-neutrality in case of diffusion) and the condition $Z^2 \ll m_1/m_2$ are assumed.

In this section we assume that the electrons make many gyrations in a time interval between effective collisions (while in the next section such an assumption will be made both for electrons and ions).

First of all it will be proved that under these conditions interference terms with coefficient α can be ignored. When electrons do not collide in a period of gyration they have a drift velocity $cB^{-1}\mathbf{E}^0 \times \mathbf{b}$ ($\mathbf{b} \equiv \mathbf{B}/B$) with respect to the coordinate system moving with the flow $\mathbf{v}_1$ of ions or the mean flow $\mathbf{v}$. Here $\mathbf{E}^0$ is the electric field in this coordinate system, $\mathbf{E}^0 = \mathbf{E} + c^{-1}\mathbf{v} \times \mathbf{B}$. This electron drift does not cause any conduction of heat. We have therefore

$$\mathbf{J} = n_2 e c B^{-1} \mathbf{b} \times (\mathbf{E} + c^{-1}\mathbf{v} \times \mathbf{B}) \text{ and } \mathbf{q} = 0 \quad (4.1)$$

for $\text{grad } T = 0$. (It should be remembered that $\mathbf{q}$ is the reduced heat flow excluding the convection heat.) Hence $\alpha = 0$ at the limit of free gyration of electrons; and, for weak interactions, the terms with α can be neglected, the tensor α^2 being sufficiently smaller than the tensor $T\lambda\gamma$.

(a) D^{II} and σ^{II}

At the limit of vanishing interaction D^{II} takes a definite value, which will be calculated in the following. We choose a coordinate system where the flow $\mathbf{v}_1$ of ions (and therefore $\mathbf{v}$ also) vanishes.

When the electric field does not exist in this coordinate system, $\mathbf{E} + c^{-1}\mathbf{v} \times \mathbf{B} = 0$, the flow $\mathbf{v}_2$ of electrons is simply

$$\mathbf{v} = \frac{ckT}{B} \frac{1}{-en_2} \mathbf{b} \times \text{grad } n_2 \quad (4.2)$$

at the limit of vanishing interaction, a proof being given in the following. The component D^{II} , which is defined by the relation

$$\mathbf{v}_2 - \mathbf{v}_1 = -\frac{n_1 + n_2}{n_1 n_2} D^{II} \mathbf{b} \times \text{grad } n_2,$$

is therefore

$$D^{II} = \frac{n_1}{n_1 + n_2} \frac{ckT}{eB}. \quad (4.3)$$

Proof of (4.2): In terms of the distribution function $f_2(\mathbf{c}_2, \mathbf{r})$ of the electron velocity $\mathbf{c}_2$ at a position $\mathbf{r}$, the flow $\mathbf{v}_2$ is determined by

$$\mathbf{v}_2 = \frac{1}{n_2} \int \mathbf{c}_2 f_2(\mathbf{c}_2, \mathbf{r}) d\mathbf{c}_2. \quad (4.4)$$

When electrons gyrate many times during a time interval between successive collisions, the function f_2 is equal to a Maxwellian distribution with respect to the position of the guiding center,

$$\mathbf{r} + \mathbf{a}_2 \text{ where } \mathbf{a}_2 \equiv \omega_2^{-1} \mathbf{c}_2 \times \mathbf{b}.$$

Thus

$$\begin{aligned} f_2(\mathbf{c}_2, \mathbf{r}) &= f_2^0(\mathbf{c}_2, \mathbf{r} + \mathbf{a}_2) \\ &= f_2^0(\mathbf{c}_2, \mathbf{r}) [1 + \mathbf{a}_2 \cdot \text{grad} \ln n_2] \\ &= f_2^0(\mathbf{c}_2, \mathbf{r}) [1 + \omega_2^{-1} \mathbf{c}_2 \cdot \mathbf{b} \times \text{grad} \ln n_2], \end{aligned} \quad (4.5)$$

where

$$f_2^0(\mathbf{c}_2, \mathbf{r}) = n_2 \left(\frac{m_2}{2\pi kT} \right)^{3/2} \exp \left(-\frac{m_2 c_2^2}{2kT} \right), \quad (4.6)$$

n_2 being the number density of guiding centers of electrons at the position $\mathbf{r}$. Substituting (4.5) into (4.4) we obtain

$$\begin{aligned} v_2 &= \frac{\mathbf{b} \times \text{grad} \ln n_2}{\omega_2} \cdot \int \mathbf{c}_2 \mathbf{c}_2 \frac{f_2^0}{n_2} d\mathbf{c}_2 \\ &= \frac{\mathbf{b} \times \text{grad} \ln n_2}{\omega_2} \int_0^\infty \frac{1}{3} c_2^2 \left(\frac{m_2}{2\pi kT} \right)^{3/2} \\ &\quad \times \exp \left(-\frac{m_2 c_2^2}{2kT} \right) 4\pi c_2^2 d\mathbf{c}_2 \\ &= \frac{\mathbf{b} \times \text{grad} \ln n_2}{\omega_2} \frac{kT}{m_2}, \end{aligned}$$

the final expression being equal to (4.2).

The non-diagonal element of the electric conductivity is given by the relation (3.15):

$$\sigma^{II} = \frac{Ze^2}{kT} (n_1 + n_2) D^{II} = \frac{en_2 c}{B}. \quad (4.7)$$

This result agrees with (4.1).

(b) D^I and σ^I

The diagonal element D^I of the coefficient of diffusion perpendicular to the magnetic field appears when there is an interaction between an ion and electron.

The guiding center $\mathbf{r}_0$ of an ion with the velocity $\mathbf{c}_1$ at the position $\mathbf{r}$ is given by

$$\mathbf{r}_0 = \mathbf{r} + \omega_1^{-1} (\mathbf{c}_1 \times \mathbf{b}),$$

where ω_1 is the gyration frequency of the ions:

$$\omega_1 = ZeB/m_1 c.$$

For an increment in ion velocity, $\Delta \mathbf{c}_1$, due to the interaction with surrounding electrons in a time interval Δt , the displacement of the guiding center is given by

$$\Delta \mathbf{r}_0 = \omega_1^{-1} (\Delta \mathbf{c}_1 \times \mathbf{b}).$$

Here Δt is taken to be much larger than the time characteristic of fluctuation of the inter-

action, but it must be much smaller than the ion gyration period. Taking average in regard to the ion velocity and the interaction with surrounding electrons we have

$$\frac{1}{\Delta t} \langle |\Delta \mathbf{r}_0|^2 \rangle_{\Delta v} = \frac{1}{\omega_1^2} \frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\Delta v}. \quad (4.8)$$

Now, (3.14) can be written in the form

$$\mathbf{v}_1 - \mathbf{v}_2 = -\frac{n_1 + n_2}{n_2} D \frac{1}{n_1} \text{grad} n_1$$

and the diagonal element of the coefficient $(n_1 + n_2) n_2^{-1} D$ is given by⁹⁾

$$\frac{n_1 + n_2}{n_2} D^I = \frac{1}{4} \frac{1}{\Delta t} \langle |\Delta \mathbf{r}_0|^2 \rangle_{\Delta v}.$$

Hence we obtain

$$D^I = \frac{1}{4} \frac{n_2}{n_1 + n_2} \frac{1}{\omega_1^2} \frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\Delta v}. \quad (4.9)$$

The diagonal element σ^I of the electric conductivity is calculated, by use of (3.15), to be

$$\begin{aligned} \sigma^I &= Ze^2 (kT)^{-1} (n_1 + n_2) D^I \\ &= \frac{1}{4} \frac{n_1}{kT} \left(\frac{Ze}{\omega_1} \right)^2 \frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\Delta v}. \end{aligned} \quad (4.10)$$

The evaluation of $(\Delta t)^{-1} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\Delta v}$ can be performed along a line quite similar to the previous paper¹⁰⁾. The increment in ion velocity $\Delta \mathbf{c}_1$ is given by

$$\Delta \mathbf{c}_1 = \frac{1}{m_1} \int_0^{\Delta t} \tilde{\mathbf{F}}(\tau) d\tau$$

where $\tilde{\mathbf{F}}(\tau)$, the force acting on the ion at time τ , is sum of contributions from all the surrounding electrons. Then under the assumption that the force due to an electron is independent of force due to other electrons, we get

$$\begin{aligned} \frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\Delta v} &= \frac{1}{m_1^2} \iiint [\mathbf{F}(0) \times \mathbf{b}] \\ &\quad \cdot [\mathbf{F}(t) \times \mathbf{b}] f_2 d\mathbf{c}_2 d\mathbf{r} dt, \end{aligned} \quad (4.11)$$

where $\mathbf{F}(t)$ is force due to an electron at time t . The electron is assumed to be located at $\mathbf{r}$ and to have velocity $\mathbf{c}_2$ at time 0 in the absence of the interaction and f_2 is the velocity distribution function for electrons, namely

$$f_2 = n_2 \left(\frac{m_2}{2\pi kT} \right)^{3/2} \exp \left(-\frac{m_2 c_2^2}{2kT} \right). \quad (4.12)$$

When the asymptotic expression for the case $\ln(kTl_D/Ze^2) \gg 1$ is required, it is sufficient to make integration of (4.11) over the domain

of "weak interaction without correlation", namely $t_s \leq |t| \leq t_p$. Here t_p , the period of plasma oscillation, and t_s , the mean time of passage through a sphere of strong interaction, are given by

$$t_p \approx \left(\frac{m_2}{kT}\right)^{1/2} l_D \text{ and } t_s \approx \left(\frac{m_2}{kT}\right)^{1/2} \frac{Ze^2}{kT}.$$

When coordinate origin is taken at position of the ion, $F(0)$ and $F(t)$ are given by

$$F(0) = \frac{Ze^2 \mathbf{r}}{|\mathbf{r}|^3}, \quad F(t) = Ze^2 \frac{\mathbf{r} + \mathbf{s}(t, \mathbf{c}_2)}{|\mathbf{r} + \mathbf{s}(t, \mathbf{c}_2)|^3}$$

where $\mathbf{s}(t, \mathbf{c}_2)$ is the displacement of the electron during time t . The integration with respect to $\mathbf{r}$ can be performed using integration by parts and gives the result

$$\int \left(\frac{\mathbf{r}}{|\mathbf{r}|^3} \times \mathbf{b} \right) \cdot \left(\frac{\mathbf{r} + \mathbf{s}}{|\mathbf{r} + \mathbf{s}|} \times \mathbf{b} \right) d\mathbf{r} = \frac{8\pi}{3} \frac{1}{|s|} \left[1 + \frac{1}{2} P_2(\cos \theta) \right] \quad (4.13)$$

where P_2 is the Legendre polynomial of the order 2 and $\cos \theta = \mathbf{b} \cdot \mathbf{s}/|\mathbf{s}|$.

Since the effect of the interaction with the ion on the motion of electron is negligibly small in the integration domain, we have

$$|\mathbf{s}(t, \mathbf{c}_2)| = [2(c_\perp/\omega_2)^2(1 - \cos \omega_2 t) + c_\parallel^2 t^2]^{1/2} \quad (4.14)$$

and

$$\cos^2 \theta = 1 + 2(c_\perp/c_\parallel)^2(1 - \cos \omega_2 t)/(\omega_2 t)^2 \quad (4.15)$$

where $c_\parallel$ and $c_\perp$ denote the parallel and perpendicular components of the electron velocity with respect to the magnetic field. Then the integration with respect to $\mathbf{c}_2$ is performed, resulting

$$\begin{aligned} & \iint [\mathbf{F}(0) \times \mathbf{b}] \cdot [\mathbf{F}(t) \times \mathbf{b}] f_2 d\mathbf{c}_2 d\mathbf{r} \\ &= \frac{16\pi}{3} \frac{1}{|t|} n_2 (Ze^2)^2 \left(\frac{m_2}{2\pi kT} \right)^{1/2} \left\{ \frac{\tanh^{-1} Y}{Y} \right. \\ & \quad \left. + \frac{1}{4Y^2} \left[\frac{3-Y^2}{Y} \tanh^{-1} Y - 3 \right] \right\} \end{aligned}$$

where

$$Y \equiv \left[1 - \frac{2(1 - \cos y)}{y^2} \right]^{1/2} \text{ and } y \equiv \omega_2 t.$$

Thus we have the final result:

$$\begin{aligned} & \frac{1}{\Delta t} \langle |\Delta \mathbf{c}_1 \times \mathbf{b}|^2 \rangle_{\text{Av}} \left[\frac{16}{3} n_2 kT \frac{m_2}{m_1^2} \left(\frac{2\pi kT}{m_2} \right)^{1/2} \right. \\ & \quad \times \left(\frac{Ze^2}{kT} \right)^2 \Big]^{-1} = \ln(t_p/t_s) + \int_0^{\omega_2 t_p} \left[\frac{\tanh^{-1} Y}{Y} - 1 \right. \\ & \quad \left. + \frac{1}{4Y^2} \left(\frac{3-Y^2}{Y} \tanh^{-1} Y - 3 \right) \right] \frac{dy}{y}. \end{aligned}$$

The right-hand side is equivalent to

$$\begin{aligned} & \ln(t_p/t_s) \quad \text{for } \omega_2 t_p \lesssim 1 \\ & \ln(t_p/t_s) + \frac{3}{4} [\ln(\omega_2 t_p)]^2 \quad \text{for } \omega_2 t_p \gtrsim 1. \end{aligned} \quad (4.16)$$

It should be noted that the limiting expression $(3/4)[\ln(\omega_2 t_p)]^2$ can be derived in an elementary way¹¹⁾.

(c) η^I and η^{II}

As regards electric resistivity, (3.10) reduces to

$$\eta^I = \sigma^I (\sigma^I)^{-2}, \quad \eta^{II} = -(\sigma^{II})^{-1}$$

since $(\sigma^I)^2 \ll (\sigma^{II})^2$ for weak interactions.

§ 5. Thermal Conduction

The thermal conductivity λ will be treated under the assumption that both electrons and positive ions make many gyrations between effective collisions.

(a) Expression for λ^I

When collisions can be neglected entirely the reduced heat flow $\mathbf{q}$ is given by

$$\mathbf{q} = \sum_{j=1}^2 \frac{1}{2} m_j \int c_j^2 f_j(\mathbf{c}_j, \mathbf{r}) d\mathbf{c}_j \quad (5.1)$$

in terms of the distribution function $f_j(\mathbf{c}_j, \mathbf{r})$. Here function f_j is equal to a Maxwellian distribution f_j^0 with respect to position of the guiding center $\mathbf{r} + \mathbf{a}_j$ where

$$\mathbf{a}_j = \omega_j^{-1} \mathbf{c}_j \times \mathbf{b},$$

ω_j being the gyration frequency. Thus

$$\begin{aligned} f_j(\mathbf{c}_j, \mathbf{r}) &= f_j^0(\mathbf{c}_j, \mathbf{r} + \mathbf{a}_j) \\ &= f_j^0(\mathbf{c}_j, \mathbf{r}) \left[1 + \left(\frac{m_j c_j^2}{2kT} - \frac{5}{2} \right) \right. \\ & \quad \left. \times \mathbf{a}_j \cdot \text{grad} \ln T \right], \end{aligned} \quad (5.2)$$

where it has been taken into account that the number density n_j is inversely proportional to the temperature T . Substituting (5.2) into (5.1) we have

$$\mathbf{q} = -\frac{5}{2} \sum_j \frac{n_j (kT)^2}{m_j} \mathbf{b} \times \text{grad} \ln T. \quad (5.3)$$

Since λ^{II} is defined by

$$\mathbf{q} = \lambda^{II} \mathbf{b} \times (-\text{grad } T)$$

we finally obtain

$$\lambda^{II} = -\frac{5}{2} k^2 T \sum_j \frac{n_j}{m_j \omega_j}. \quad (5.4)$$

It is important to note that all $\mathbf{v}_j$ vanish,

$$\mathbf{v}_j = \frac{1}{n_j} \int \mathbf{c}_j f_j(\mathbf{c}_j, \mathbf{r}) d\mathbf{c}_j = 0,$$

as it should since there is no interference between thermal and electric conductions (cf. the third paragraph of Section 4).

(b) *Expression for λ*

When the magnetic field is so strong that the electrons and ions make many free gyrations, only collisions between ions determine the heat conduction in the direction of the temperature gradient which is assumed to be perpendicular to the strong magnetic field. (Because an effective collision between ions causes an energy transfer proportional to the square of the ion gyration radius, which is nearly m_1/m_2 times the square of the electron gyration radius. The collision frequency between electrons or between ion and electron is only $(m_1/m_2)^{1/2}$ times the collision frequency between ions.) The ion gyration radius is usually larger than the Debye shielding length, and the collisions between ions can be treated in a way similar to collision integrals in the kinetic theory of gases. In fact the coefficient of thermal conduction in this case has been obtained by Fradkin⁵⁾, who solved the Boltzmann equation. Here we shall develop a short discussion without using the Boltzmann equation.

Let $\mathbf{e}$ denote the unit vector in the direction of $\text{grad } T$. Then

$$\frac{m_1}{2}(c_1'^2 \mathbf{a}_1' + \bar{c}_1'^2 \bar{\mathbf{a}}_1' - c_1^2 \mathbf{a}_1 - \bar{c}_1^2 \bar{\mathbf{a}}_1) \cdot \mathbf{e}$$

or

$$\frac{m_1}{2\omega_1}(c_1'^2 \mathbf{c}_1' + \bar{c}_1'^2 \bar{\mathbf{c}}_1' - c_1^2 \mathbf{c}_1 - \bar{c}_1^2 \bar{\mathbf{c}}_1) \cdot (\mathbf{b} \times \mathbf{e})$$

indicates energy transferred in the direction of $\mathbf{e}$ by a collision with initial velocities $\mathbf{c}_1, \bar{\mathbf{c}}_1$ and final velocities $\mathbf{c}_1', \bar{\mathbf{c}}_1'$. The component q of the heat flow in the direction $\mathbf{e}$ is

$$q = \frac{1}{2} \frac{m_1}{2\omega_1} \iiint (c_1'^2 \mathbf{c}_1' + \bar{c}_1'^2 \bar{\mathbf{c}}_1' - c_1^2 \mathbf{c}_1 - \bar{c}_1^2 \bar{\mathbf{c}}_1) \cdot (\mathbf{b} \times \mathbf{e}) f_1(\mathbf{c}_1, \mathbf{r}) f_1(\bar{\mathbf{c}}_1, \mathbf{r}) \times g b d b d \varepsilon d \mathbf{c}_1 d \bar{\mathbf{c}}_1, \quad (5.5)$$

where g is the relative speed $|\mathbf{c}_1 - \bar{\mathbf{c}}_1|$, b is the impact parameter, and ε is the azimuthal angle of the orbit of relative motion.

The expression (5.5) can be transformed, by virtue of (5.2) for $j=1$, into

$$q = |\text{grad } \ln T| \frac{m_1}{12\omega_1^2} \iiint (c_1'^2 \mathbf{c}_1' + \bar{c}_1'^2 \bar{\mathbf{c}}_1' - c_1^2 \mathbf{c}_1 - \bar{c}_1^2 \bar{\mathbf{c}}_1) \cdot \left[\mathbf{c}_1 \left(\frac{m_1 c_1^2}{2kT} - \frac{5}{2} \right) + \bar{\mathbf{c}}_1 \left(\frac{m_1 \bar{c}_1^2}{2kT} - \frac{5}{2} \right) \right] \times f_1^0(\mathbf{c}_1) f_1^0(\bar{\mathbf{c}}_1) g b d b d \varepsilon d \mathbf{c}_1 d \bar{\mathbf{c}}_1. \quad (5.6)$$

Introducing the center-of-mass velocity $\mathbf{G} = \frac{1}{2}(\mathbf{c}_1 + \bar{\mathbf{c}}_1)$ and the relative velocity $\mathbf{g} = \mathbf{c}_1 - \bar{\mathbf{c}}_1$ and integrating with respect to $\mathbf{G}$, we can reduce (5.6) to

$$q = -|\text{grad } \ln T| \frac{m_1}{6} \frac{n_1^2}{\omega_1^2} \left(\frac{m_1}{4kT} \right)^{3/2} \times \sqrt{\pi} \iint g^6 \exp \left(-\frac{m_1 g^2}{4kT} \right) (1 - \cos^2 \theta) g b d b d g \quad (5.7)$$

where θ is the angle of diffraction in the orbit of relative motion. Evaluating the integral in (5.7) we obtain the thermal conductivity across a strong magnetic field,

$$\lambda^i = \frac{8}{3} k \frac{kT}{\omega_1^2 m_1} n_1^2 \left(\frac{\pi kT}{m_1} \right)^{1/2} \left(\frac{Z^2 e^2}{kT} \right)^2 \ln \frac{kT l_D}{Z^2 e^2}, \quad (5.8)$$

which agrees with Fradkin's⁵⁾ expression.

According to (5.8) λ^i/k is equal to the square of ion gyration radius, $kT/m_1 \omega_1^2$, multiplied by the ion-ion collision frequency per unit volume, as it should.

References

- 1) H. Maecker and Th. Peters: *Z. Phys.* **144** (1956) 586.
- 2) T. Kihara: *J. Phys. Soc. Japan* **14** (1959) 128.
- 3) T. G. Cowling: *Proc. Roy. Soc. A*, **183** (1945) 453.
- 4) R. Landshoff: *Phys. Rev.* **76** (1949) 904.
- 5) E. S. Fradkin: *J. Exp. Theor. Phys. (U.S.S.R.)* **32** (1957) 1176.
- 6) S. I. Braginskii: *J. Exp. Theor. Phys. (U.S.S.R.)* **33** (1957) 459.
- 7) I. Prigogine: *Etude Thermodynamique des Phenomenes Irreversible* (Liège, 1947) 101.
- 8) See, for example, S. R. de Groot: *Thermodynamics of Irreversible Processes* (North-Holland, 1953), or J. Meixner and H. G. Reik: *Handb. d. Phys.* III2 (Springer, 1959).
- 9) For example, S. Chandrasekhar: *Rev. Mod. Phys.* **15** (1943) 1.
- 10) T. Kihara, Y. Midzuno, K. Sakuma and T. Shizume: *J. Phys. Soc. Japan* **15** (1960) 684.
- 11) T. Kihara: *J. Phys. Soc. Japan* **14** (1959) 1751.

Flow of a Condensing Vapour with Heat Exchange

By Keishiro NIU

*Department of Physics, University of Osaka Prefecture,
Sakai near Osaka*

(Received January 27, 1960)

An analysis is given for the flow of a condensing vapour with heat exchange which passes through a pipe of constant cross-sectional area. The solutions obtained here are the extension of Chiarulli-Dressler's ones, and the general features of the phenomena are illustrated by an application to a flow with definite initial conditions. The two figures given by numerical calculations show distinctly the differences of the flow patterns between the supersonic and subsonic cases.

§ 1. Introduction

In the historical development of hydrodynamics the theory of condensation has played a particular role. Indeed, the theory of condensation was frequently applied to the investigations on the shock-like phenomena occurred near the throat of a diverging nozzle which was used to obtain the supersonic flow in the laboratory.^{1,2)} Namely, it was applied to the phenomena caused exclusively by the adiabatic expansion of the vapour, as well as to the cases in which the amount of condensation occurred in the flow was so small that the gas characteristics of the fluid were predominant. In the later development of the theory by Chiarulli and Dressler, however, a different order of magnitude of the condensation was treated, namely, their assumed conditions were such that the total condensation took place³⁾. On the other hand, the flows of non-condensing vapours in pipes have been extensively treated by means of the one-dimensional approach⁴⁾.

Thus the remaining problem is to develop an analysis which may be applicable to both an intermediate stage and the limiting cases mentioned above. In order to see especially what changes would appear in the flow pattern due to the condensation phenomena caused by the thermal conduction, we have discussed the effects due only to the heat exchange at the pipe walls, leaving aside the phenomena caused by the adiabatic change of the vapour. We shall show in the following that the present problem can be treated by a method quite analogous to that employed by Chiarulli and Dressler. In order to simplify the considerations and calculations, following three assump-

tions have been made. First, the flow is assumed to be one-dimensional, namely, the fluctuations of temperature, pressure and velocity in the inviscid fluid flow passing through a pipe of constant cross-sectional area are supposed to be negligible in each section. The second assumption is that the supersaturated state does not occur in the supersonic flow as well as in the subsonic one, though under this assumption we miss the condensation shock which is one of the most interesting condensation phenomena in the supersonic flow and which is expected to appear not only in the adiabatic expansion but also in our case.

One of our purposes of extending the theory of condensation is to observe the qualitative effects that the phase transition of the fluid from vapour to liquid caused by the heat exchange brings about in the states of flow. Thereby, neglecting complicated changes due to congelation, we assume lastly that the flow consists at most of the two phases of gas and liquid.

Under these assumptions, the application of conservation laws of mass, momentum and energy to the states on both the end sections of the pipe leads to the extended Rnachine-Hugoniot relations which include the heat removal effect. In § 2, we shall treat these conservation laws.

The next step is to derive the solutions for the two-phase flow where the vapour and the liquid coexist. We shall show in § 3 that if we assume the fluid to be ideal, the solutions are obtained by a method similar to that used by Chiarulli and Dressler.

In § 4 we shall continue the solutions ob-

tained in §3 to ones for the cases of the vapour alone or the liquid alone at the exit section of the pipe. We shall also discuss the meaning of the double signs appeared in the derived expressions.

Finally, in §5, we shall illustrate the behaviour of the flow by applying the solutions to a example with such initial conditions as $P=125$ cmHg, $T=200^\circ\text{C}$ and $M=1$.

§ 2. Conservation Laws

In order to study the process of bringing about the condensation by means of the heat conduction through the walls, we now consider the case when the steam alone enters the initial section of a uniform pipe and there is no friction at the walls. It is assumed that the cooling effect by the heat removed through the walls gives rise to the condensation of a part of the vapour until it reaches the exit section, thus the mixture of the vapour and the liquid issuing from the exit section.

Then the rate of the mass flow, m , satisfies the equation of continuity:

$$m_v + m_L = m_e = m \quad (1)$$

Here, as well as in the following, the subscript e refers to the values at the entrance section, while the subscripts V and L refer to those for the vapour and liquid at the exit section respectively.

When there are no losses of momentum, the equation of motion becomes

$$AP + m_v U_v + m_L U_L = A_e P_e + m U_e, \quad (2)$$

where A is the cross-sectional area of the passage, P the pressure and U the velocity.

The energy equation is given by

$$m_v \left(H_v + \frac{1}{2} U_v^2 \right) + m_L \left(H_L + \frac{1}{2} U_L^2 \right) = m \left(H_e + \frac{1}{2} U_e^2 \right) - h, \quad (3)$$

where h is defined as the heat quantity removed from the fluid through the pipe walls between the two end sections and H represents the enthalpy per unit mass.

The equations so far given do not involve the condition that the cross-sectional area of the pipe is constant, which is represented by the equation:

$$A_v + A_L = A_e = A. \quad (4)$$

Since we have assumed that the flow is one-

dimensional, we have

$$U_v = U_L = U, \quad (5)$$

notwithstanding that the condensation occurs.

Lastly, if we use the densities, m_v , m_L and m_e can be rewritten as:

$$m_v = A_v U_v \rho_v, \quad (6)$$

$$m_L = A_L U_L \rho_L, \quad (7)$$

$$m_e = m = A U_e \rho_e. \quad (8)$$

§ 3. Solutions of the Conservation Equations

In this section, we shall derive the solutions of the conservation equations for a case in which

$$0 < m_L < m, \text{ or } 0 < m_v < m. \quad (9)$$

By virtue of (1), (5) and (8), the equation of motion (2) is reduced to

$$P + U_p U \rho_e = P_e + U_e^2 \rho_e. \quad (10)$$

If we introduce a quantity m' such that

$$m' = m/A = \rho_e U_e, \quad (11)$$

the above equation (10) can be rewritten as:

$$P + m' U = P_e + m' U_e. \quad (12)$$

The equation of energy (3) also takes the following form:

$$m H_L + \frac{1}{2} m U^2 + m_v (H_v - H_L) = m \left(H_e + \frac{1}{2} U_e^2 \right) - h. \quad (13)$$

To eliminate the the unknown variable m_v from this equation, we use, in addition to (6) and (8), the following relation:

$$A_v = \frac{A(m' - \rho_L U)}{\rho_L U(\rho_v/\rho_L - 1)}, \quad (14)$$

which comes (1) and (4). Then the reduced energy equation becomes

$$H_L + \frac{1}{2} U^2 + \frac{\rho_v(m' - \rho_L U)}{\rho_L m'(\rho_v/\rho_L - 1)} (H_v - H_L) = H_e + \frac{1}{2} U_e^2 - \frac{h}{m}. \quad (15)$$

Since, however, an inequality:

$$\rho_v/\rho_L \ll 1 \quad (16)$$

holds for a rather wide range of conditions, the term ρ_v/ρ_L in Eq. (15) can be neglected in comparison with unity. With this approximation, Eq. (15) reduces to

$$H_L + \frac{1}{2} U^2 - \frac{\rho_v(m' - \rho_L U)}{\rho_L m'} (H_v - H_L) = H_e + \frac{1}{2} U_e^2 - h', \quad (17)$$

where

$$h' = h/m. \quad (18)$$

On the other hand, Eq. (12) gives

$$U = (P_e - P)/m' + U_e \quad (19)$$

Thus, substituting this into Eq. (17), we have

$$\begin{aligned} H_L + \frac{1}{2} \left(\frac{P_e - P}{m'} + U_e \right)^2 \\ - \left\{ 1 - \frac{\rho_L}{m'} \left(\frac{P_e - P}{m'} + U_e \right) \right\} \frac{\rho_V (H_V - H_L)}{\rho_L} \\ = H_e + \frac{1}{2} U_e^2 - h' \end{aligned} \quad (20)$$

Here, we reduce Eq. (20) to a relation giving the temperature T as a function of h' , by taking the following thermodynamic suppositions into account. Since the vapour coexists with the liquid at the exit section of the pipe in the case under consideration, the pressure is equal to the saturated vapour pressure, provided that the flow there is in equilibrium state. Namely:

$$P = P_s(T). \quad (21)$$

Another significant simplification can be carried out by making use of the assumption

that the vapour is a perfect gas, so that its density and enthalpy may be approximated respectively by

$$\rho_V = P/(RT), \quad (22)$$

and

$$H_V = C_p T, \quad (23)$$

where R is the gas constant and C_p the specific heat at constant pressure.

The remaining simplification is made by considering that for many liquids, water being a prime example, the function H_L can be approximated as a linear function of the temperature for a fairly wide range of $T^{(5)}$. We can then write

$$H_L = \kappa T + \kappa_0, \quad (24)$$

where κ is a known constant and the constant κ_0 is so chosen that the zero levels of the enthalpy for the liquid and the vapour are the same. The density of the liquid can now be considered as a function of T alone:

$$\rho_L = \rho_L(T), \quad (25)$$

which can be obtained from existing tables. By virtue of Eqs. (21)~(25), Eq. (20) becomes ultimately

$$\begin{aligned} \frac{\kappa_0 P_s(T)^2}{m'^2 P T} + \left(1 - \frac{P_e \rho_L(T)}{m'^2} - \frac{U_e \rho_L(T)}{m'} \right) \frac{\kappa_0 P_s(T)}{R T \rho_L(T)} + \left(\frac{1}{2m'^2} - \frac{C_p - \kappa}{m'^2 R} \right) P_s(T)^2 \\ - \left\{ \frac{P_e}{m'^2} + \frac{U_e}{m'} + \left(1 - \frac{P_e \rho_L(T)}{m'^2} - \frac{U_e \rho_L(T)}{m'} \right) \frac{C_p - \kappa}{R \rho_L(T)} \right\} P_s(T) + \kappa T \\ = H_e - \frac{P_e^2}{2m'^2} - \frac{P_e U_e}{m'} - \kappa_0 - h'. \end{aligned} \quad (26)$$

For each value of h' , Eqs. (26), (21), (19), (22) and (25) may be used to obtain the temperature, the velocity, the density of the vapour and the density of liquid, respectively.

§ 4. Continuation of the Solutions

The solutions derived in the preceding section for the case of mixture of two phases at the exit section of the pipe may be connected with the following two limiting cases.

(a) *Case when the fluid consists of the vapour alone.*

In this case

$$m_V = m, \quad m_L = 0, \quad (27)$$

so that the equations of continuity, motion and energy reduce respectively to

$$\rho U = \rho_e U_e = m', \quad (28)$$

$$P + m' U = P_e + m' U_e, \quad (29)$$

$$H + \frac{1}{2} U^2 = H_e + \frac{1}{2} U_e^2 - h'. \quad (30)$$

Here, both the equation of state (22) and the equation of enthalpy (23) still hold. Thus, making use of these equation, we have

$$P = m' R T / U, \quad (31)$$

$$T = \left(H_e + \frac{1}{2} U_e^2 - h' - \frac{1}{2} U^2 \right) / C_p, \quad (32)$$

$$\begin{aligned} m' U^2 \left(1 - \frac{1}{2} R / C_p \right) - U \left(P_e + m' U_e \right) \\ + \frac{m' R}{C_p} \left(H_e + \frac{1}{2} U_e^2 - h' \right) = 0. \end{aligned} \quad (33)$$

If we introduce the following four positive constants B , C , D and E expressed in terms of the initial conditions:

$$B = m' \left(1 - \frac{1}{2} R/C_p \right), \quad C = P_e + m' U_e,$$

$$D = m' R/C_p, \quad E = H_e + \frac{1}{2} U_e^2, \quad (34)$$

Eq. (33) yields

$$U = \frac{C \pm \sqrt{C^2 + 4BD(h' - E)}}{2B}. \quad (35)$$

In order to inquire the meaning of the double signs in the above equation, we have to express U and h' in terms of the Mach number M for a perfect gas, which is given by

$$M = U/\sqrt{\gamma R T}, \quad (36)$$

γ being as usual the adiabatic exponent. Substituting (22), (28) and (36) into Eq. (29), we have

$$P + \gamma P M^2 = \text{const},$$

or, alternatively,

$$P \propto 1/(1 + \gamma M^2). \quad (37)$$

Similarly, the temperature can be written as:

$$T \propto M^2/(1 + \gamma M^2)^2, \quad (38)$$

and therefore we have

$$\rho \propto P/T \propto (1 + \gamma M^2)/M^2. \quad (39)$$

Thus, by (28) and (39),

$$U \propto 1/\rho \propto M^2/(1 + \gamma M^2). \quad (40)$$

On the other hand, after similar reductions, Eq. (30) gives

$$H_e + \frac{1}{2} U_e^2 - h' \propto \frac{M^2 \left\{ 1 + \frac{1}{2} (\gamma - 1) M^2 \right\}}{(1 + \gamma M^2)^2}. \quad (41)$$

Now, differentiation of the right-hand sides of Eqs. (40) and (41) with respect to M yields

$$2M/(1 + \gamma M^2)^2 \quad \text{and} \quad M(1 - M^2)/(1 + \gamma M^2)^3,$$

respectively. The former is always positive for any value of M , but the latter is negative unless $0 < M < 1$. This fact implies that the increase of h' induces the speed-up of the fluid in the supersonic flow (the plus sign in Eq. (35) being therefore used for this case) and *vice versa* in the subsonic flow (the minus sign being used for this case).

(b) *Case when all the vapour condenses in the pipe.*

The solutions for this case were obtained by Chiarulli and Dressler. We now have

$$m_v = 0, \quad m_L = m, \quad (42)$$

so that the equation of motion (2) reduces to

$$P + m' U = P_e + m' U_e. \quad (43)$$

If we use the same approximation as (16), we get

$$U = m'/\rho_L \ll U_e = m'/\rho_e, \quad (44)$$

and Eq. (43) is rewritten as:

$$P = P_e + m' U_e. \quad (45)$$

On the other hand, substituting (18), (24) and (42) into Eq. (3) and neglecting the quadratic terms of U , we have

$$T = (H_e + \frac{1}{2} U_e^2 - \kappa_0 - h')/\kappa. \quad (46)$$

This is in perfect agreement with the corresponding Chiarulli-Dressler's solution in which $H_v = H_e$, $U_v = U_e$, $V_v = 1/\rho$, $h_w = h$, $c_p = \kappa$ and $c_0 = \kappa_0$. For this case the density ρ and the velocity U are also given respectively by Eq. (25) and (28).

§ 5. Numerical Results and Conclusions

Using the solutions of the conservation equations, we have carried out numerical calculations for an example with initial conditions such that $P_e = 152 \text{ cmHg} = 2.02 \times 10^6 \text{ dyne cm}^{-2}$, $T_e = 200^\circ \text{C} = 473^\circ \text{K}$ and $M = 1$. The last one means that the flow starts with the sonud velocity, from which we obtain $U_e = 5.39 \times 10^4 \text{ cm sec}^{-1}$, $\rho_e = 9.27 \times 10^{-4} \text{ gram cm}^{-3}$, $m' = 5.00 \times 10 \text{ gram cm}^{-2} \text{ sec}^{-1}$. By making use of the ordinary thermodynamic constants and relations, it can be approximately determined that $P_s(T) = 4.98 \times 10^{11} \exp(-4.89 \times 10^3/T) \text{ dyne cm}^{-2}$, $H_L = 4.19 \times 10^7 T - 3.17 \times 10^{10} \text{ erg gram}^{-1}$ and $\rho_L = \text{const} = 1 \text{ gram cm}^{-3}$. The constants employ-

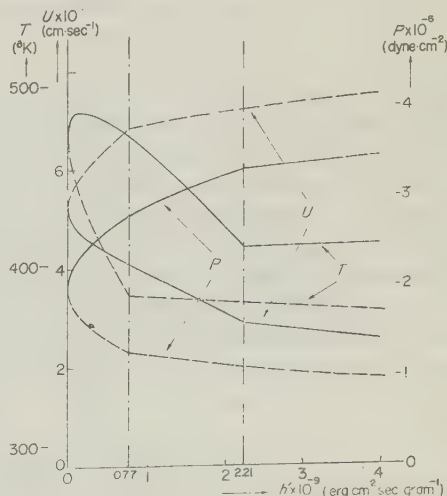


Fig. 1.

ed for the vapour are: $R=4.61 \times 10^6$ erg gram⁻¹ deg⁻¹, $C_p=1.86 \times 10^7$ erg gram⁻¹ deg⁻¹ and $\gamma=1.33$.

The results of the calculations are shown in Figs. 1 and 2. In Fig. 1, the relations of the velocity, the temperature and the pressure *versus* the removed heat quantity are shown by full-line curves for the subsonic flow, and by broken-line curves for the supersonic one, while in Fig. 2, the same relations for the subsonic case are shown for larger values of h' . (The scales of ordinates and abscissae are different from each other in these two figures. It will be seen from these curves that the saturation is reached approximately at the values of $h'=0.77 \times 10^9$ erg sec gram⁻¹ in the supersonic case and at $h'=2.21 \times 10^9$ erg sec gram⁻¹ in the case of subsonic flow. (Chain lines show the positions of these values of h' .) Another interesting conclusion is also afforded by these curves, namely, the condensation phenomena cause the abrupt change in the slopes of every curve at the above positions, yet, with the exception of the curve for temperature,

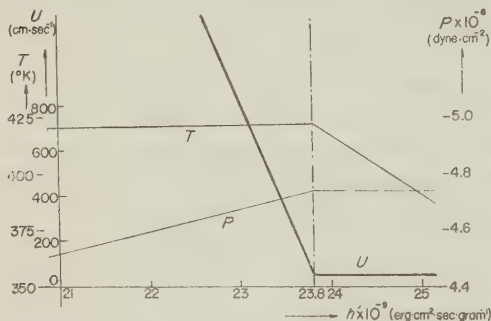


Fig. 2.

they make the curves take monotonous tendencies analogously to the case of flow of the vapour alone. The temperature for the subsonic branch has a maximum in the earlier state of the vapour alone, and in spite of the heat removal effect from the fluid, it increases again slightly in the region associated with the condensation phenomena.

In the subsonic case, $h'=23.8 \times 10^9$ erg sec gram⁻¹ is the sufficient value (indicated by

a chain-line in Fig. 2) to condense all the vapour. Thenceforth, the completely condensed liquid flows downstream with the decrease in temperature, both the pressure and the velocity being however kept at constant values. On the other hand, it seems that complete condensation cannot be realized actually in the supersonic flow. In order to substantiate this intuitive reasoning, can we derive the fact that the removed heat of amount of $h'=26.9 \times 10^9$ erg sec gram⁻¹ will transform the whole fluid to the liquid phase at the very state of zero Kelvin's temperature and zero pressure. At this unrealizable limiting state, $A_L=0$ in spite of $m_L=m$, because the decrease in temperature causes more rapid diminution of the pressure besides the increase of condensation, and as a consequence, it enlarges the area through which the vapour flows.

When the cooling effect for the supersonic flow brings out the transition to the subsonic state, curves also suggest the occurrence of a shock wave, particularly accompanied with the partial evaporation or condensation for the region $0.77 \times 10^9 < h' < 23.8 \times 10^9$ erg sec gram⁻¹ and with the whole phase change of the remaining vapour for $23.8 \times 10^9 < h' < 26.9 \times 10^9$ erg sec gram⁻¹, provided that it is possible.

The author wishes to express his cordial thanks to Prof. S. Tomotika not only for his encouragement but also for his kind inspection of the manuscript. He is also indebted to Prof. T. Simasaki and to Dr. K. Hida for their useful discussions.

References

- 1) P. P. Wegener: J. Appl. Phys. **25** (1954) 1485.
- 2) H. Wakeshima: J. Phys Soc. Japan **10** (1955) 141.
- 3) P. Chiarulli and R. F. Dressler: J. Appl. Phys. **28** (1957) 990.
- 4) L. Howarth: *Modern Developments in Fluid Dynamics, High Speed Flow*, vol. I (Oxford, 1953) 205.
- 5) K. Shiba: *Butsuri Josu Hyo* (Iwanami, 1949) 146 (in Japanese).

Selbstzündung des *n*-Hexan-Luft-Gemisches in Stosswellen

Von Kunio TERA0

Institut für physikalische Chemie der Universität Göttingen

(Received February 2, 1960)

The ignition lag of *n*-hexane-air mixtures in shockwaves was measured, under different conditions, in order to analyze its fluctuations statistically. The probabilities of ignition of the mixtures were thus calculated. The ignition was considered to consist of two steps: the initiation reaction and the secondary reaction. The activation energies of both these steps were calculated in each case. These values were then used in an attempt to explain some aspect of the mechanism of ignition.

§ 1. Einleitung

Nach der Theorie, die zuerst von K. Zuber¹⁾ und von M. von Laue²⁾ aufgestellt und nachher von M. Hirata³⁾ weiter entwickelt wurde, sollten die makroskopischen Größen einer Erscheinung eine gewisse Schwankung haben, die mit einer kleinen mikroskopischen Änderung zunimmt, wie z. B. bei Elektrofunkens, dem Bruch der Gläser⁴⁾ und Metalle⁵⁾, oder Reibungserscheinungen⁶⁾. Diese Schwankung entsteht natürlich teilweise durch empirische Fehler, aber der größte Teil ist aus physikalischen Gründen unvermeidlich, und auch wenn man es ganz genau untersucht hätte, würde man doch die Schwankung haben.

Wenn man z. B. die Induktionszeit einer Erscheinung, in der einige mikroskopischen Änderungen entstehen und zur makroskopischen Größe wachsen, in zahlreichen Fällen unter derselben Bedingung messen könnte, würde man eine Verteilungskurve der Induktionszeit bekommen, wie sie in Bild 1 dargestellt wird.

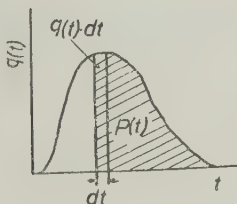


Bild 1.

Unterstellt man, daß

$P(t)$: die Wahrscheinlichkeit dafür ist, daß die Induktionszeit größer als eine beliebige Zeit t ist,

$q(t) \cdot dt$: das Häufigkeitsverhältnis dafür ist, daß die Induktionszeit zwischen t

und $t + dt$ liegt,

$\mu(t)$: die Wahrscheinlichkeit ist, wie oft die Erscheinung in der Zeiteinheit vorkommt,

dann ist $P(t) = \int_t^\infty q(t) \cdot dt$.

Andererseits ist $P(t) \cdot \mu(t) \cdot dt = -dP$ und

$$\mu(t) = -d\{\ln P(t)\}/dt \quad (1)$$

Also kann man damit aus der Verteilungskurve die Wahrscheinlichkeit $\mu(t)$ ersehen.

Da in der Entzündung von Gasen⁷⁾ auch ein solcher Fall vorliegt, d. h. eine kleine Reaktion der Moleküle zur Flamme wächst, könnte man hierbei auch die Theorie anwenden. Dabei kann man dieses genauso betrachten, wie K. Zuber es sich zuerst beim Elektrofunkens vorgestellt hat. Wenn nämlich ein brennbares Gas in irgendeinem Zustand wird, z. B. auf eine hohe Temperatur, bei der es sich entzünden kann, sollte es erst überall mit Startreaktionen beginnen, die davon über einige weitere Reaktionen zur Flamme führen. Diese Startreaktionen können nur weiter zur Flamme führen, wenn sie andere aktivierte Moleküle immer wieder treffen und sich reagieren, ohne durch Stöße mit nicht aktivierten Molekülen oder durch andere Störungen ihre Energie zu verlieren. Es ist aber ganz zufällig, ob eine Startreaktion aktivierte Moleküle weiter trifft und sich reagiert, oder nicht mehr. Wenn eine von den gebliebenen Startreaktionen am schnellsten zur Flamme wächst, dann beherrscht sie die Induktionszeit, aber wenn sie irgendwo unterwegs durch Stöße mit nicht aktivierten Molekülen stirbt, muß sie ihre Stelle der zweiten Startreaktion geben, die ihr anschließt. Damit kann die zweite die Induktionszeit beherrschen. Dabei ist die Induktions-

zeit länger als die von der ersten. Wenn die zweite auch unterwegs stirbt, wird die Geschichte wiederholt und die dritte beherrscht die Induktionszeit, die noch länger sein muß als die von der zweiten. So wird die Geschichte bis zur Entzündung immer wieder wiederholt. Wenn alle Startreaktionen unterwegs sterben, kann das Gas nicht mehr entzünden. Deshalb muß die Induktionszeit keinen bestimmten Wert haben, sondern eine Schwankung. Von der Schwankung kann man, wie gesagt, nach Gl. 1 die Wahrscheinlichkeit der Entzündung in der Zeiteinheit $\mu(t)$ bekommen, die deswegen die Produkt von der Wahrscheinlichkeit für die Startreak-

tion α und der für die Entwicklung zur Entzündung β sein.

$$\mu(t) = \alpha \cdot \beta \quad (2)$$

Nach dieser Idee wollte ich die Selbstzündung des *n*-Hexan-Luft-Gemisches untersuchen. Dabei muß man die Temperatur des Gemisches möglichst schnell erhöhen, und hierzu ist die Stoßwellenmethode sehr geeignet.

§ 2. Versuchsmethode

Das für das Experiment hergestellte Stoßrohr ist aus 4 Stahlvierkantrohren zusammengesetzt. Jedes hat etwa die Länge von 1 m und einen Querschnitt von $3 \times 3 \text{ cm}^2$.

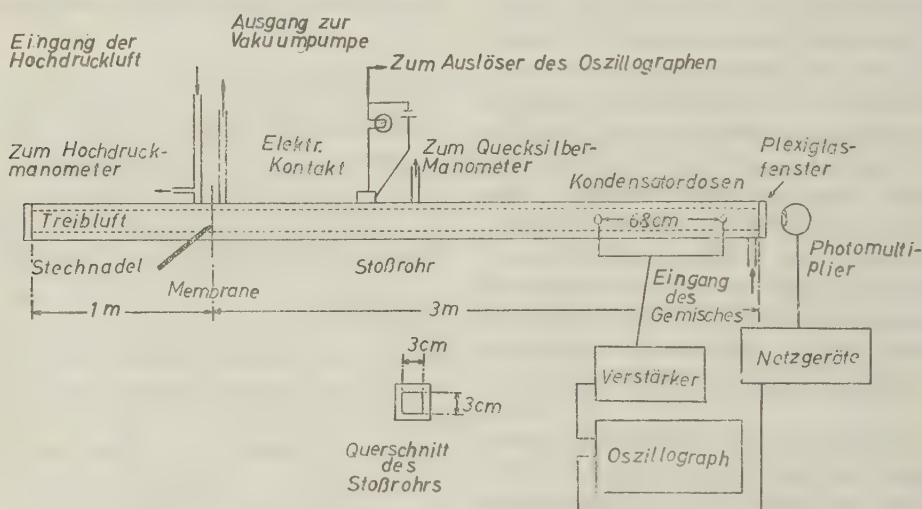


Bild 2. Schema der Versuchsvorrichtung.

In das erste Stück wird die Hochdrucktreibluff und in die andern das *n*-Hexan-Luft-Gemisch eingeführt. Als Membrane zwischen Hoch- und Tiefdruckteilen wurden Aluminiumfolien von 0,3 oder 0,2 mm Stärke benutzt, deren Zahl je nach dem Treibdruck geändert wurde. Die Membrane wurde von einer Stechnadel zerbrochen, wenn die Bedingungen erfüllt waren. In das letzte Stück waren zwei Kondensatordosen mit einem Abstand von 68 cm eingestzt, um die Druckänderung der Stoßwelle als Elektrokapazitätsänderung in einen Oszillographen weiterleiten zu können. Die Druckempfangsmembrane jeder Kondensatordose hat 8 mm Durchmesser und 0,5 mm Stärke. Am Ende des Stoßrohrs war eine Plexiglasplatte eingesetzt, so daß die Entflammung von draußen mit einem Photo-

multiplier gemessen werden konnte. Das *n*-Hexan-Luft-Gemisch wurde durch einen Doppelsättiger hergestellt, und in das hintere Stoßrohr ein- und vom vorderen ausgeführt. Das Gemisch wurde mit 2 bis 3 Liter je Minute und 12 bis 7 Minuten laufen gelassen, nach der Füllung erst mit einer Vakuumpumpe abgepumpt und dann dicht zugemacht, um den Druck von 90 bis 180 mm Hg je nach den Bedingungen zu halten.

Der gebrauchte Oszillograph ist ein Tektronix Typ 545, dessen Auslöser durch die Abbrechung einer elektrischen Schaltung betätigt wurde, die mit einer von der Stoßwelle bewegten Membrane mit der Wand des Stoßrohrs fest gebunden war. Die beiden Kondensatordosen sind parallel verbunden, so daß die Zeiten, in denen die Stoßwelle an der er-

sten und zweiten Dose vorbeiläuft, auf einer Linie aufgezeichnet werden.

Bild 3a zeigt einen Druckverlauf der Stoßwelle, der nur mit der ersten Dose gemessen wurde, und Bild 3b zeigt einen solchen, der mit der zweiten Dose gemessen wurde. Wenn man die beiden Dose gleichzeitig parallel benutzt, dann bekommt man einen Druckverlauf wie Bild 3c zeigt, in dem der erste und

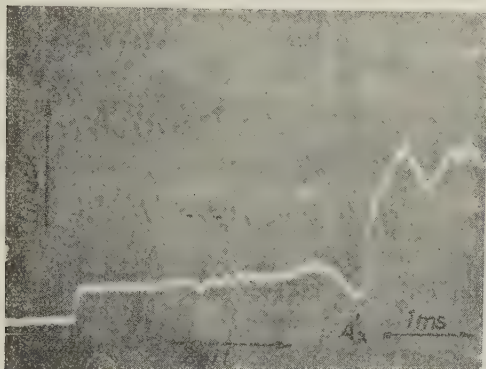


Bild 3a. Druckverlauf der Stoßwelle an der ersten Kondensatordose.

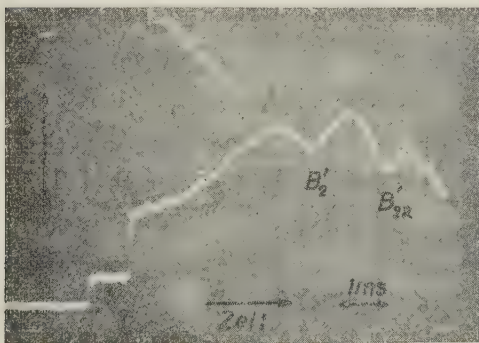


Bild 3b. Druckverlauf der Stoßwelle an der zweiten Kondensatordose.

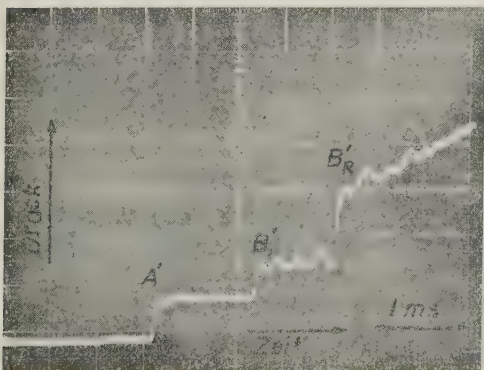


Bild 3c. Druckverlauf der Stoßwelle, der gleichzeitig von den beiden Kondensatordosen gemessen wurde.

der zweite Druckverlauf überlagert waren. Bild 4 zeigt diesen Druckverlauf in Bezug auf die Zeit. Wie das Bild zeigt, kann man mit dieser Methode nicht nur die Geschwindigkeit der einfallenden Stoßwelle, sondern auch die der reflektierenden Stoßwelle messen. Der Meßfehler ist weniger als 1%, wenn die Zeitauslösung des Oszillographen auf 5 cm/1 Millisekunde gestellt ist.

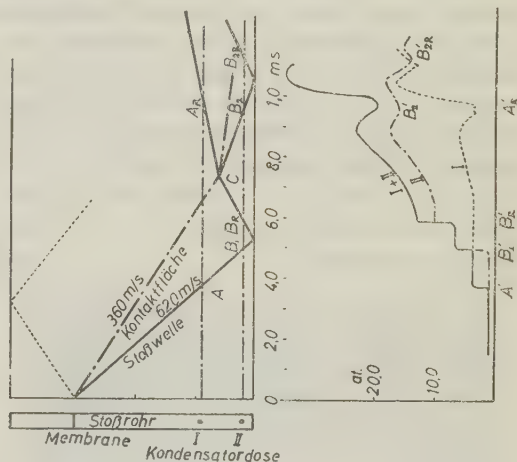


Bild 4. Druckverlauf der Stoßwelle an der Dose (I), an der Dose (II), und der überlagerte Druckverlauf (I+II) im Zusammenhang mit der Stoßfront.

Da die Rückwelle sich in etwas eineinhalb Millisekunde nach der Reflektion an die Endwand an der Kontaktfläche stößt und wieder teilweise reflektiert, kann man den Zustand darum kaum ausrechnen. Da ich die Entzündung nur in der ersten Rückwelle messen wollte, durfte ich es nur in dieser Zeit, d.h. 1,5 Millisekunde nach der Reflektion an der Endwand, zur Entzündung kommen lassen.

Um die Entzündungszeit zu messen, war außen beim Fenster am Ende des Stoßrohres ein Photomultiplier eingesetzt, der weiter in den Oszillographen eingeführt war. Mit zwei Strahlen des Oszillographen, die gleichzeitig laufen, kann man den Druckverlauf der Stoßwelle, von dem man gleich die Geschwindigkeit und Zeit ausrechnen kann, in der die Stoßwelle an der Endwand des Stoßrohres ankommt, und die Entzündungszeit gleichzeitig messen. Damit kann man weiter die Induktionszeit, d.h. den Zeit-abstand zwischen der Reflektionszeit an der Endwand und der Entzündungszeit messen. (Bild 5)

Die Temperatur und den Druck der Rück-

welle kann man aus der Geschwindigkeit der Stoßwelle berechnen⁸⁾⁹⁾, wenn das Verhältnis der spezifischen Wärme bekannt ist. Das Verhältnis der spezifischen Wärme habe ich nach der Tabelle des American Petroleum Institut Research Project 44 berechnet.

Die Temperatur der Rückwelle änderte sich zwischen 700°K und 950°K, und der Druck immer fast konstant, d.h. 3,0 bis 3,5 at. gehalten. Unter einer bestimmten Bedingung habe ich meistens über 80 Mal denselben Versuch gemacht, die Bedingung, z.B. Mischungsverhältnis, Druckverhältnis des Hoch- und Tiefdruckteils und Zimmertemperatur ($\pm 1^\circ\text{C}$) möglichst genau konstant haltend. Zu jedem Versuche wurde die Geschwindigkeit der Stoßwelle auch immer gemessen, die immer dieselbe sein muß.

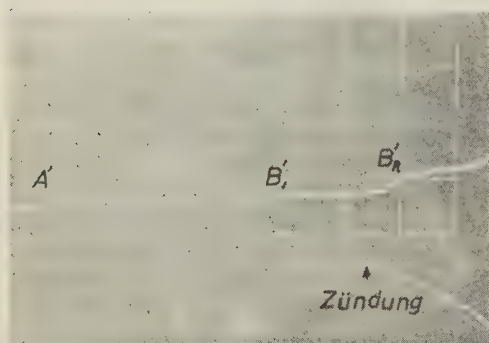


Bild 5. Druckverlauf und Entzündung.

§ 3. Versuchsergebnisse

Bild 6 zeigt ein Beispiel der Verteilungskurve der Induktionszeit bei der Selbstzündung des *n*-Hexan-Luft-Gemisches in Stoßwellen. Nach so einer Verteilungskurve kann man nach der Gl. 1 die Wahrscheinlichkeit der Entzündung in einer Zeiteinheit berechnen, aber dabei wird das Volumen des Gemisches nach der Reflektion an der Endwand mit der Zeit immer größer, welches für die Entzündung in Frage kommen soll. Nämlich nach der Reflektion läuft die reflektierende Stoßwelle immer weiter zurück und mit der Rückwelle nimmt der Bereich der Hochtemperatur immer mehr zu. Deshalb muß man diese Volumenänderung dabei berücksichtigen.

Nimmt man jetzt folgendes an:

$\mu(t)$: Wahrscheinlichkeit der Entzündung in einer Millisekunde und in einem Mol,

V : Volumen des Gemisches, das in der hohen Temperatur zur Entzündung gebracht wird,

V_m : Volumen eines Mols des Gemisches,

A : Querschnittsfläche des Stoßrohres,

D_2 : Geschwindigkeit der Rückwelle

t : Zeit nach der Reflektion an der Endwand,

$$\mu(t) \cdot \frac{V}{V_m} = -\frac{d(\ln P)}{dt}$$

$$\mu(t) \cdot \frac{A \cdot D_2 \cdot t}{V_m} = -\frac{d(\ln P)}{dt}$$

Wenn $\mu(t)$ konstant ist, dann ist

$$\frac{1}{2} \cdot \mu(t) \cdot \frac{A \cdot D_2}{V_m} \cdot t^2 = -\ln P(t) + C$$

$$\mu(t) = -2 \cdot V_m \frac{\ln P_1 - \ln P_2}{A \cdot D_2 \cdot (t_1^2 - t_2^2)} \quad (3)$$

Wenn $\mu(t)$ wirklich konstant, d.h. unabhängig von der Zeit ist, muß die $P(t)$ -Kurve in Bezug auf t^2 immer eine Gerade sein. Bild 7 zeigt es von Bild 6 her. Es ist eine Gerade

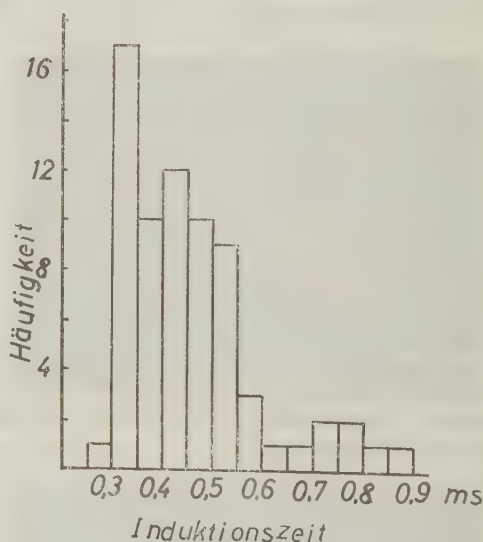


Bild 6. Verteilungskurve der Induktionszeit der Entzündung des *n*-Hexan-Luft-Gemisches bei $\lambda=1,0$ und 790°K .

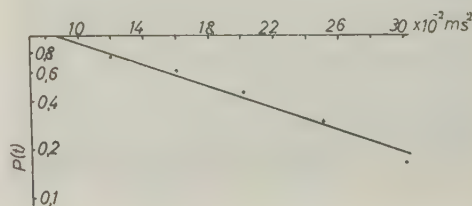


Bild 7. $\ln P(t)$ in Bezug auf Quadrat der Induktionszeit.

Tabelle I

Machsche Zahl der einfallenden Stoßwelle	Temperatur °K	Druck at.	$\mu(t)$ Mol ⁻¹ ·msec ⁻¹	τ msec	$\bar{t}_g$ msec
2,20	730	3,45	410	0,435	0,73
2,29	790	3,22	1 274	0,300	0,46
2,44	873	3,50	5 880	0,195	0,25

Tabelle II

(Mischungsverhältnis 0,6, Konzentration 1,33% Vol.)

Machsche Zahl	Temperatur °K	Druck at.	$\mu(t)$ Mol ⁻¹ ·msec ⁻¹	τ msec	$\bar{t}_g$ msec
2,195	765	3,45	2 020	0,298	0,38
2·37	870	3·38	13 700	0,15	0,18

Tabelle III

(Mischungsverhältnis 0,3)

Machsche Zahl	Temperatur °K	Druck at.	$\mu(t)$ Mol ⁻¹ ·msec ⁻¹	τ msec	$\bar{t}_g$ msec
2,195	798	3,58	6 900	0,217	0,25
2·37	890	3·20	58 500	0,072	0,086

Tabelle IV

(Mischungsverhältnis 0,15)

Machsche Zahl	Temperatur K°	Druck at	$\mu(t)$ Mol ⁻¹ ·msec ⁻¹	τ msec	$\bar{t}_g$ msec
2,14	780	3,47	6 550	0,20	0,23
2,33	865	3,10	59 800	0,06	0,079

und ihre Neigung gegen t^2 ist die Wahrscheinlichkeit der Entzündung in einer Millisekunde und einem Mol.

Tabelle 1 zeigt die Versuchsergebnisse für das stöchiometrische Gemisch, d.h. bei einem Mischungsverhältnis 1,0 und Konzentration 2,2% Vol.. Dabei bedeutet τ die Zeitlänge, in der keine Entzündung entsteht, und $\bar{t}_g$ die durchschnittliche Induktionszeit.

Die Induktionszeit der Entzündung hat normalerweise 2 Teile. In dem ersten Teil zündet es sich überhaupt nicht, und in dem andern schwankt die Induktionszeit. Die durchschnittliche Induktionszeit der Selbstzündung für eine bestimmte Gemischmenge, z.B. N Mol unter adiabatischer Kompression beträgt:

$$\tau_g = \tau + \frac{1}{N \cdot \mu(t)}$$

(4)

Deswegen ist die durchschnittliche Induk-

tionszeit von der Gemischmenge abhängig, besonders bei wenigem Gemisch und niedriger Temperatur. Bild 8 zeigt den Zusammen-

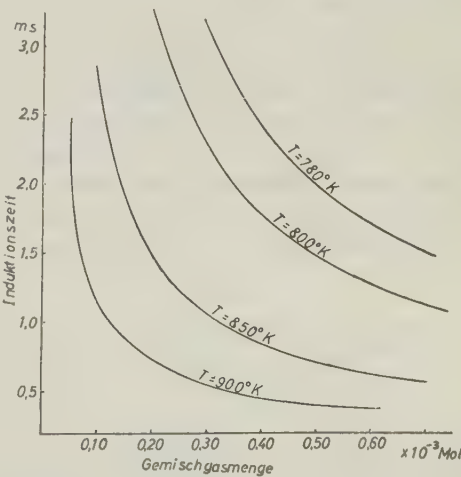


Bild 8.

hang zwischen der durchschnittlichen Induktionszeit, Gemischmenge und Temperatur eines stöchiometrischen *n*-Hexan-Luft-Gemisches. Wenn man deshalb die Induktionszeit der Entzündung bei mehrer Gasmenge untersucht, z.B. ein noch größeres Stoßrohr benutzt, wird die Schwankung geringer und die Induktionszeit kürzer und nährt sich zu τ asymptotisch.

Wie schon gesagt, soll $\mu(t)$ aus 2 Teilen bestehen, d. h. aus der Wahrscheinlichkeit α , wieviel Startreaktion am Anfang vorhanden ist, und aus der Wahrscheinlichkeit β dafür, daß sich die Startreaktion zur Entzündung entwickelt.

$$\mu(t) = \alpha \cdot \beta \quad (2)$$

Unter derselben Bedingung soll α proportional der Zahl der Moleküle sein, die in die Reaktion kommen, nämlich der Menge des Gemisches. Mit dieser Wahrscheinlichkeit α ist $\mu(t)$ proportional der Menge des Gemisches. Im übrigen, wenn die Aktivierungsenergie der Startreaktion E_1 ist, soll die Wahrscheinlichkeit der Entzündung auch proportional $e^{-(E_1/RT)}$ sein.

Dagegen hängt β nur von dem Zustand der Moleküle einer Startreaktion. Nimmt man E_2 als die Aktivierungsenergie der Sekundärreaktion und W als die Wärme an, die aus der ersten und der anschließenden Reaktion ausgeführt und der Sekundärreaktion zugegeben wird, dann soll β proportional $e^{-(E_2-W)/RT}$ sein. Also

$$\mu(t) = A \cdot e^{-(E_1+E_2-W)/RT} \quad (5)$$

Dabei ist A ein Konstant.

Die Zeitlänge τ , in der keine Entzündung entsteht, ist noch unklar, aber man könnte annehmen, daß es die Zeitlänge ist, die die Entzündung mindestens gebraucht, d. h. in der die Reaktion am günstigsten und schnellsten vor sich geht. Daß diese Zeitlänge von der Gasmenge unabhängig ist, könnte auch es bedeuten. Dann soll es auch proportional $e^{(E_2-W)/RT}$ sein. Nämlich es hängt von der

Reaktionsgeschwindigkeit ab, die am schnellsten ist.

$$\tau = B \cdot e^{(E_2-W)/RT} \quad (6)$$

B ist auch ein Konstant.

Von der Neigung von $\ln \mu(t)$ und $\ln \tau$ in Bezug auf $1/T$ kann man nach der Gleichung 5 und 6 E_1+E_2-W und E_2-W und weiter E_1 ausrechnen. Bild 9 zeigt die Kurven von $\ln \mu(t)$ und $\ln \tau$ in Bezug auf $1/T$. Hieraus ersieht man gleich, daß je magerer das Gemisch ist, desto mehr die Neigung von $\ln \mu(t)$ und $\ln \tau$, und A und B auch sind.

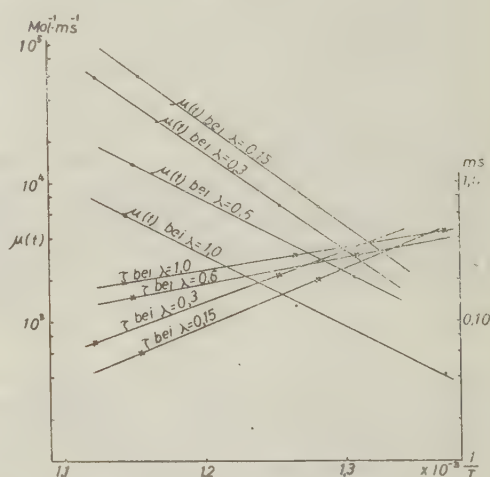


Bild 9. $\ln \mu(t)$ und $\ln \tau$ in Bezug auf $1/T$ für verschiedene Mischungsverhältnisse.

Tabelle 5 zeigt E_1+E_2-W , E_2-W , E_1 , A und B für verschiedene Mischungsverhältnisse. Aus diesen Ergebnissen kann man gleich ersehen, daß jede Aktivierungsenergie der Startreaktion in jedem Falle immer fast gleich etwa 16,3 Kcal/Mol ist. Das bedeutet nämlich, daß die erste Reaktion für verschiedene Mischungsverhältnisse immer dieselbe ist, und nur die anschließende Sekundärreaktion anders ist.

§ 4. Weitere Analyse

Bei der Selbstzündung des *n*-Hexan-Luft-

Tabelle V

Mischungsverhältnis	E_1+E_2-W Kcal/Mol	E_2-W Kcal/Mol	E_1 Kcal/Mol	A	B
1,0	24,0	7,0	17,0	$67,5 \times 10^6$	$3,5 \times 10^{-3}$
0,6	24,6	8,9	15,7	$22,4 \times 10^9$	$8,5 \times 10^{-4}$
0,3	32,7	16,4	16,3	$60,6 \times 10^{11}$	$8,0 \times 10^{-6}$
0,15	35,3	19,0	16,3	$50,7 \times 10^{12}$	$9,0 \times 10^{-7}$

Gemisches handelt es sich hauptsächlich um *n*-Hexan- und Sauerstoffmoleküle. Ein *n*-Hexanmoleküle trifft direkt ein aktiviertes O₂-Molekül oder indirekt, d. h. vermittelt einer oder mehrer Sauerstoffverbindungen, immer wieder und erzeugt zum Schluß sich teilend CO₂ und H₂O.

Bei der ersten Stufe müßten einige *n*-Hexanmoleküle auf O₂-Moleküle treffen und sich reagieren, den nachkommenden O₂-Molekülen oder den bei der Reaktion entstandenen Sauerstoffverbindungen die Reaktionswärme übergebend, oder sie bei sich behaltend. Hieran schließt sich die weitere Reaktion. Dabei könnten sich die vier folgenden Fälle ergeben:

(1) Das einmal reagierte *n*-Hexanmolekül mit der Reaktionswärme trifft immer wieder auf ein aktiviertes O₂-Molekül, reagiert sich und kommt dadurch, daß die Temperaur durch die Reaktion hoch genug wird, zur Entflammung. Dabei bleibt die Reaktionswärme immer beim *n*-Hexanmolekül.

(2) Die bei der Reaktion entstandene Sauerstoffverbindung mit der Reaktionswärme fliegt und trifft nur ein oder wenige bestimmte *n*-Hexanmoleküle, welches oder welche die erste Reaktion hinter sich haben und dann weiter zur Entflammung kommen. Die Reaktionswärme wird durch die Sauerstoffverbindungen oder Zwischenprodukte transportiert.

(3) Die O₂-Moleküle, die schon einmal reagierte *n*-Hexanmoleküle treffen und daher die Reaktionswärme bekommen, treffen auch nur ein oder weniger bestimmte *n*-Hexanmoleküle, welche die erste Reaktion schon hinter sich haben und sich dann damit weiter zur Entflammung reagiert. Die Reaktionswärme wird durch O₂-Moleküle transpotiert.

(4) Alle drei Fälle treffen zusammen. In jedem Falle muß ein *n*-Hexanmolekül direkt oder indirekt immer wieder treffen, während die Reaktionswärme zur weiteren Reaktion übertragen wird, obwohl sie durch vergebliche Stöße immer geringer wird.

Ist

- ε : die Aktivierungsenergie sich zu teilen und mit einem Sauerstoffmolekül zu reagieren
- ε₁ : die Aktivierungsenergie zu einer Startreaktion
- ε₂ : die Aktivierungsenergie zu einer Sekundärreaktion

- w : die Reaktions wärme, die zu einer Sekundärreaktion aufgenommen wird
- n : die Reaktionsstufenzahl, d. h. die Stoßzahl eines *n*-Hexanmoleküls mit einem O₂-oder demsprechenden Sauerstoffverbindung, das sich damit reagieren kann
- n₁ : die Reaktionsstufenzahl bei der Startreaktion
- n₂ : die Reaktions stufenzahl bei der Sekundärreaktion
- ν_h die Molekulardichte des *n*-Hexan
- ν_o die Molekulardichte des Sauerstoffs
- Z : die gesamte Stoßzahl der *n*-Hexanmoleküle mit O₂ Molekülen je Millisekunde für ein Mol Gemisch,

dann ist die Wahrscheinlichkeit dafür, daß nur eine Bindung eines *n*-Hexanmoleküls auseinandergeht und mit einem O₂ Molekül direkt oder indirekt reagiert :

$$w = a \cdot e^{-(\varepsilon/RT)}$$

a ist auch eine Wahrscheinlichkeit dafür, daß ein O₂-Molekül ein bestimmtes *n*-Hexanmolekül trifft. Wenn das *n*-Hexanmolekül noch öfter z. B. *n* Mal kontinuierlich ein aktiviertes O₂-Molekül (direkt oder indirekt) trifft, muß die Wahrscheinlichkeit dafür

$$(w)^n = (a \cdot e^{-(\varepsilon/RT)})^n = a^n \cdot e^{-(n\varepsilon/RT)} \tag{7}$$

sein. Die Wahrscheinlichkeit dafür, daß irgendein *n*-Hexanmolekül in einem Mol-Gemisch wie oben ein O₂-Molekül *n* Mal je Millisekunde trifft und sich reagiert, ist

$$Z \cdot a^n \cdot e^{-(n\varepsilon/RT)}$$

Wenn man den Vorgang in die Startreaktion und die Sekundär-Reaktion teilt, muß es

$$Z \cdot a^{n_1+n_2} e^{-(n_1\varepsilon_1+n_2\varepsilon_2-n_2w)/RT}$$

sein, und gleich μ(t) sein, solange in jeder Stufe dieselbe Reaktion vor sich geht. Von Gl. 5 ist

$$A \cdot e^{-(E_1+E_2-W)/RT} = Z \cdot a^{n_1+n_2} \cdot e^{-(n_1\varepsilon_1+n_2\varepsilon_2-n_2w)/RT} \tag{8}$$

Daher

$$\begin{aligned} E_1 &= n_1 \cdot \varepsilon_1 \\ E_2 &= n_2 \cdot \varepsilon_2 \\ W &= n_2 \cdot w \\ A &= Z \cdot a^{n_1+n_2} \end{aligned}$$

Unter der Voraussetzung, daß ein aktiviertes O₂-Molekül, wenn es ein *n*-Hexanmolekül trifft, sich reagieren und verschwinden muß,

kann die Wahrscheinlichkeit dafür, daß nur ein O_2 -Molekül ein bestimmtes n -Hexanmolekül trifft, in der nullten Annäherung proportional $1/\nu_h$ sein, solange es nicht beschränkt ist, wie oft es andere Moleküle trifft. Andererseits ist Z proportional $\nu_h \cdot \nu_0$. Daraus ergibt sich

$$A = C \cdot \nu_h \cdot \nu_0 \left(\frac{1}{\nu_h} \right)^{n_1 + n_2} \tag{10}$$

Wenn man ν_0 konstant annehmen kann, weil es im Vergleich mit ν_h sehr groß und mit der Konzentration sich kaum ändert, kann man $n_1 + n_2$ von der Neigung der Kurve $\ln A$ in Bezug auf $\ln(1/\nu_h)$ bekommen. Wenn man die Kurve als eine Gerade annehmen kann, ist es 5 bis 6. Für B von der Gl.6 könnte es auch einen ähnlichen Zusammenhang geben. Dabei kommt nur die Sekundärreaktion in Frage.

$$B = C' \cdot \left(\frac{1}{\nu_h} \right)^{-n_2}$$

Genau so wie bei A kann man n_2 von der Kurve $\ln B$ in Bezug auf $\ln(1/\nu_h)$ bekommen. Dabei ist n_2 4 bis 5. Deshalb $n_1=1$, oder 2 und $n_2 = 4$ oder 5.

Tabelle VI

λ	$n_1=1,$	ε_1	3	$\varepsilon_2 - W$	5
		2, Kcal/Mol		$n_2=4,$ Kcal/Mol	
1,0	17,0	8,5	5,7	1,8	1,4
0,6	15,7	7,9	5,2	2,2	1,8
0,3	16,3	8,2	5,4	4,1	3,3
0,15	16,3	8,2	5,4	4,8	3,8

Ueber $E_2 - W$ für verschiedene Konzentrationen läßt sich noch nichts sagen, aber wenn man sich in der nullten Annäherung $E_2 - W$ für eine beliebige Konzentration durch Interpolation vorstellen könnte, kann man für alle Konzentrationen die Linien von $\mu(t)$ und τ in Bezug auf $1/T$ bekommen, damit man alle Induktionszeiten je nach dem Zustand errechnen kann. Bild 10 zeigt einige Linien von $\ln \mu(t)$ und $\ln \tau$ für verschiedene Konzentrationen des n -Hexan in Bezug auf $1/T$; die theoretisch ausgerechnet wurden, und Bild 11 zeigt die durchschnittliche Induktionszeit der Selbstzündung des 0,01 Mol n -Hexan-Luft-Gemisches in Bezug auf die Konzentration mit Parameter T . Wie das Bild zeigt, ist das Mischungsverhältnis, das die minimale

Induktionszeit hat, je nach der Temperatur anders. Je höher die Temperatur ist, desto magerer ist das Gemisch, das die minimale Induktionszeit hat.
Es ist aber schwer zu sagen, daß $n_1 + n_2$ für verschiedene Konzentrationen immer konstant ist. Es gibt noch eine Möglichkeit, daß es um so mehr wird, je magerer das Gemisch wird, weil ein n -Hexanmolekül mehrere O_2 -Moleküle treffen kann als bei einem fettern Gemisch.

Ueber $E_2 - W$ könnte man wenigstens sagen,

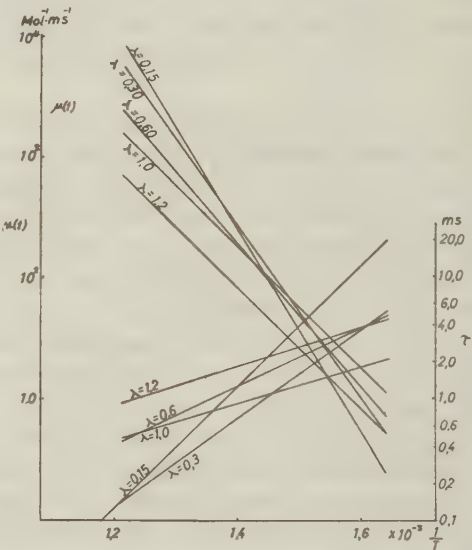


Bild 10. $\ln \mu(t)$ und $\ln \tau$ des n -Hexan-Luft-Gemisches, die theoretisch ausgerechnet wurden.

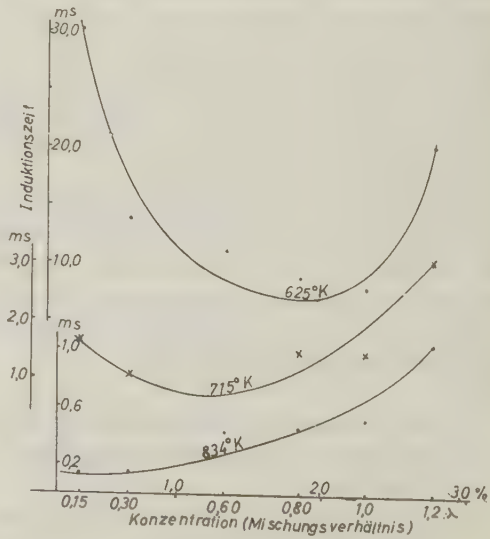


Bild 11. Theoretische durchschnittliche Induktionszeit der Entzündung des n -Hexan-Luft-Gemisches in Bezug auf Mischungsverhältnis.

daß es, wenn das magerer wird, zunimmt. Nämlich je magerer das Gemisch ist, um so geringer ist die Wärme W , weil ein Molekül mit der Reaktionswärme, entweder n -Hexan oder O_2 oder Sauerstoffverbindung, andere Moleküle als n -Hexan öfter treffen muß als bei fetterm, bis es ein anderes n -Hexanmolekül trifft, und es dann mehr Wärme verlieren muß.

§ 5. Vergleich mit anderen Arbeiten

A. Martinengo und H. Gg. Wagner¹⁰⁾ haben die Selbstzündung des n -Hexan-Luft-Gemisches unter adiabatischer Kompression

untersucht. Dabei wurde das Gemisch in einem Zylinder mit 3 cm Durchmesser von einem Kolben sehr schnell adiabatisch unter Druck gestetzt und gezündet. Nun möchte ich die damit gemessenen Induktionszeiten und die, die mit der Gleichung 4 ausgerechnet wurden, vergleichen. Dieses wird in Tabelle VII gezeigt. Dabei ist

$$\tau_{\mu} = \frac{1}{\mu(t) \times \text{Molzahl}},$$

durchschnittliche Induktionszeit
 $\tau_g = \tau_{\mu} + \tau$
und τ_e ist die empirisch gemessene Induktions-

Tabelle VII. *n*-Hexan-Luft-Gemisch bei $\lambda=1,0$

Temperatur °K	Druck at.	Molzahl 10 ⁻³ Mol	Molzahl $\times \mu(t)$ sec ⁻¹	τ_{μ} msec	τ msec	τ_g msec	τ_e msec
610	12,2	6,45	77,0	13,0	1,2	14,2	21,0
650	14,5	7,18	359,0	2,8	0,8	3,6	11,2
670	17,1	8,2	656,0	1,5	0,68	2,2	5,1
700	19,8	9,5	155,0	0,65	0,54	1,19	2,0

zeit. Die Mischung war stöchiometrisch. Wenn man nach der Gleichung $\tau_g = \text{Konstant} \times e^{E/RT} \ln \tau_g$ in Bezug auf $1/T$ zeichnet, erhält man Bild 12a. Dann kann man von der Neigung der Linie $\ln \tau_g$ die sogenannte anschauliche Aktivierungsenergie bekommen. Wie das Bild zeigt, stimmt die Energie von der theoretischen Berechnung mit der empirisch gemessenen gut überein, obwohl die Temperatur parallel etwa 40°K nach unten verschoben ist. So ein Meßfehler kann oft vorkommen,

solange die Versuchsmethode anders ist, während es relativ wenigen Fehler bei demselben Experiment gibt.

Es gibt noch eine ähnliche Arbeit von Levedahl¹¹⁾. Dabei war das Mischungsverhältnis 0,375 und ebenfalls wurde das Gemisch in einer Kompressionsmaschine adiabatisch gedrückt und gezündet. $\mu(t)$ habe ich von $\mu(t)$ bei $\lambda=0,3$ berechnet, den Unterschied der Konzentration berücksichtigend. Nach dem Unterschied von τ bei $\lambda=0,3$ und bei $\lambda=0,15$ soll der bei $\lambda=0,375$ und bei $\lambda=0,3$ nicht groß, höchsten 10% sein. Deshalb habe ich τ für $\lambda=0,375$ von denen bei $\lambda=0,3$ angenommen. Die Gemischmenge wurde vom Verdichtungsverhältnis, dem Durchmesser des Zylinders und vom Kolbenschub aus geschätzt. Dabei stimmt es vielleicht nicht genau, aber da die Menge sehr groß ist, spielt der Fehler nur eine kleine Rolle.

Bild 12b zeigt $\ln \tau_g$ und $\ln \tau_e$ in Bezug auf $1/T$. Beide Ergebnisse stimmen gut überein, und der Unterschied der Induktionszeit steht im Bereich der Schwankungen.

Durch den Vergleich mit den zwei Arbeiten ergibt sich, daß das Experiment und die theoretische Idee richtig seien. Wenn man die Energie $E_2 - W$ richtig schätzen könnte, könnte man damit theoretisch, wie Bild 10 zeigt,

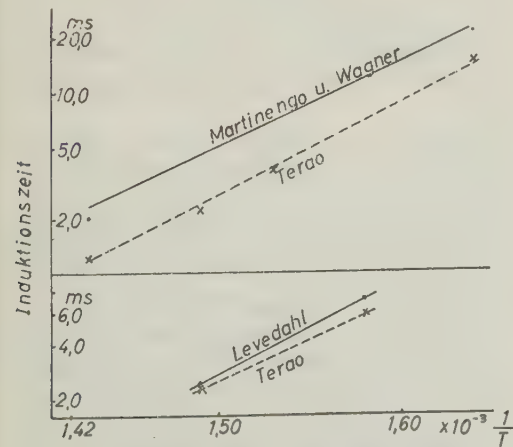


Bild 12. Induktionszeit der Entzündung des n -Hexan-Luft-Gemisches in Vergleich mit anderen Arbeiten.

Tabelle VIII. *n*-Hexan-Luft-Gemisch bei $\lambda=0,375$

Temperatur °K	Molzahl 10 ⁻³ Mol	Molzahl $\times \mu(t)$ sec ⁻¹	τ_{μ} msec	τ msec	τ_g msec	τ_e msec
632	87	1 480	0,68	4,90	5,58	7,0
671	93	6 900	0,145	2,19	2,34	2,4

$\mu(t)$ und τ ausrechnen und die durchschnittliche Induktionszeit erhalten.

§ 6. Zusammenfassung

1) Wenn man die Induktionszeit in Gasen als einen Wahrscheinlichkeitsprozess statisch betrachtet, die immer eine Schwankung hat, die nicht nur aus dem empirischen Fehler kommt, sondern auch und zwar hauptsächlich aus einem physikalischen Grund, und die deshalb unvermeidlich ist, dann erhält man aus der Schwankung eine Entzündungswahrscheinlichkeit in einer Zeit- und Mengeneinheit.

2) Die Induktionszeit der Entzündung besteht aus zwei Teilen. Der eine ist der, in dem keine Entzündung entsteht, und der andere der, in dem die Entzündungszeit immer schwankt. Der erste scheint unabhängig von der Gasmenge und abhängig von der Reaktionsgeschwindigkeit zu sein, aber der letzte hängt von der Gasmenge ab. Von den beiden könnte man die Entzündungsreaktion als zwei Reaktionen betrachten, d. h. als Start- und Sekundärreaktion. Daraus kann man die Aktivierungsenergie der Start- und Sekundärreaktion erhalten, und die Reaktionsstufenzahl vermuten.

3) Beim *n*-Hexan-Luft-Gemisch ist die Startreaktion für verschiedene Mischungsverhältnisse immer dieselbe und die Reaktionsstufenzahl (wie oft es sich mit O₂-Molekül reagiert) ist 1, oder 2. Die Aktivierungsenergie der Sekundärreaktion ist für verschiedene Mischungsverhältnisse immer anders. Je magerer das Gemisch ist, desto größer ist die Aktivierungsenergie. Es wurde die Reaktionsstufenzahl 4 oder 5 vermutet.

4) Aus der Entzündungswahrscheinlichkeit und der Zeitlänge, in der überhaupt keine Entzündung entsteht, kann man die durchschnittliche Induktionszeit je nach dem Zustand errechnen.

5) Das Mischungsverhältnis, das die minimale durchschnittliche Induktionszeit hat, ist je nach der Temperatur anders. Je niedriger die Temperatur ist, um so fetter muß das

Gemisch sein, das die minimale Induktionszeit hat.

Der Charakter der Induktionszeit der Entzündung in Gasen ist damit ziemlich klar geworden, aber es besteht noch die Frage, welche chemischen Bindungen z.B. C–H, oder C–C an der Reaktion teilnehmen, oder die Reaktionsstufenzahl, die Wärme, die die Reaktion fördert, usw. sind noch nicht ganz klar. Wenn man noch mehr Brennstoff untersucht, würde es allmählich klar werden.

Als Entzündungszeit wurde die Entflammungszeit angenommen. Wenn die Versuchsmethode anders und als Entzündungszeit anders angenommen würde, z. B. raschen Druckanstieg des Gases, kann das Ergebnis konkret etwas anders sein.

Zum Schluß danke ich Herrn Prof. Dr. W. Jost und Dr. H. Gg. Wagner für die freundliche Leitung und die guten Ratschläge für die Arbeit.

Schrifttum

1) K. Zuber: Ann. Physik (1925) 231.
2) M. von Laue: Ann. Physik (1925) 261.
3) M. Hirata: Bull. Math. Stat. **3** (1947) 57; Kikai no Kenkyu **1** (1949) 182; 231 Ooyotokeigaku (Angewandte Statistik) 1949, 11, 01.
4) N. Terao: J. Phys. Soc. Japan **8** (1953) 545, 550; **9** (1954) 879.
5) T. Yokobori: J. Phys. Soc. Japan **6** (1951) 78, 81, 404; **7** (1952) 44, 48, 122; **8** (1953) 104, 107, 265.
6) H. Nagasu: J. Phys. Soc. Japan **6** (1951) 270.
7) K. Terao: J. Phys. Soc. Japan **10** (1955) 154, 304.
8) E. E. Greene u. J. P. Toennis: Chemische Reaktion in Stosswellen, Dr. Dietrich (Steinkopff Verlag, 1959).
9) N. Manson: Propagation des Détonations et des Déflagrations dans les Mélanges Gazeux, (Edition de L'office National D'études et de Recherche Aéronautiques et L'institut francais des Petroles, 1947).
10) A. Martinengo und H. Gg. Wagner: Z. phys. Chemie Neue Folge, 1960 (Im Druck).
11) W. J. Levedahl: Fifth Symposium on Combustion, 372.

Short Notes

This section is intended to secure prompt publication of important discoveries in physics. The reports should not exceed 800 words in length. A figure of size 7 cm × 7 cm will be counted as 150 words.

J. PHYS. SOC. JAPAN **15** (1960) 1123

Magnetic Anisotropy of Chalcopyrite

By Teruo TERANISHI

*Department of Physics, Faculty of Science,
Hokkaido University, Sapporo*

(Received February 8, 1960)

Chalcopyrite, CuFeS_2 , has been known as a semiconductor¹⁾ including iron, of which we have special interest in connexion with the study of magnetism. Donnay et al.²⁾ investigated the material by neutron diffraction and found it to be antiferromagnetics at room temperature.

We have made magnetic measurements using single crystal of chalcopyrite. A disc parallel to (110)-plane is cut out from a large natural single crystal found at Arakawa mine, Japan. According to chemical analysis this crystal contains 33.54 weight % of copper, 31.7% iron, 33.9% sulphur and 0.90% of insoluble matter.

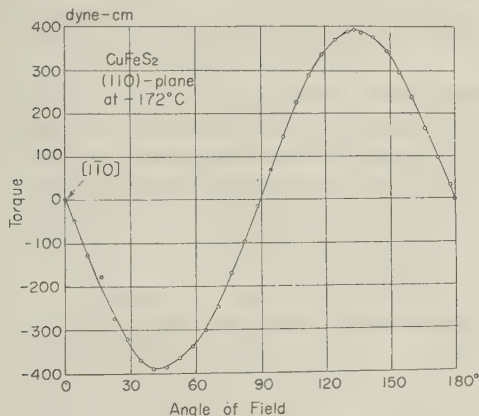


Fig. 1. Torque curve of chalcopyrite.

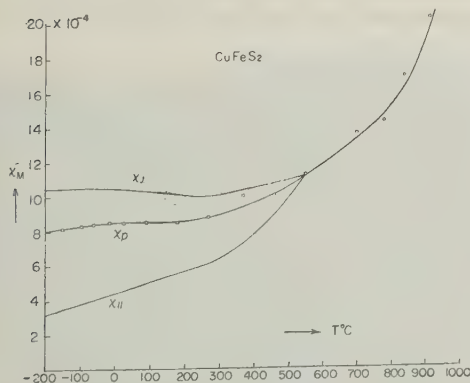


Fig. 2. Temperature variations of susceptibilities of chalcopyrite.

The torque in a uniform magnetic field of 10200 Oe is measured at -172°C and room temperature by a torque magnetometer. At both temperatures the torque shows two-fold symmetry as shown in Fig. 1. The easy direction of the torque is $[1\bar{1}0]$. The variation of maximum torque with the square of magnetic field strength is found to be linear. The maximum torque decreases nearly linearly with rising temperature and at about 550°C the torque vanishes. This uniaxial torque is caused from the difference between two principal susceptibilities, $\chi_{//}$ and $\chi_{\perp}$, of the crystal in which the magnetic moments are presumably aligned antiferromagnetically and directed along $[001]$ direction. The Néel temperature of this antiferromagnetism is considered to be 550°C where the torque vanishes.

The variation with temperature of powder susceptibility of this crystal is shown in Fig. 2 denoted as χ_p . From powder susceptibility and the torque we can calculate $\chi_{//}$ and $\chi_{\perp}$. Temperature dependencies of these susceptibilities are shown in Fig. 2, too. $\chi_{\perp}$ is nearly independent upon the temperature and $\chi_{//}$ goes down to zero as the temperature decreases to absolute zero, just as the theory of antiferromagnetism suggests.

Powder susceptibility continues to increase above the Néel temperature. This is probably due to the decomposition of the specimen into other substances one of which (for example, FeS) has high magnetic susceptibility. When chalcopyrite in the evacuated silica tube is quenched from 900°C , we can observe a considerable amount of sulphur adhering on the wall of silica tube. But we cannot detect other substances than chalcopyrite by X-ray diffraction method.

The author wishes to thank Prof. Miyahara for valuable discussions and Prof. Harada for delivering the single crystal of chalcopyrite.

References

- 1) C. H. L. Goodman and R. W. Douglas: *Physica* **20** (1954) 1107. I. G. Austin, C. H. L. Goodman and A. E. Pengelly: *J. Electrochem. Soc.* **103** (1956) 609.
- 2) G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliot and J. M. Hastings: *Phys. Rev.* **112** (1958) 1917.

J. PHYS. SOC. JAPAN **15** (1960) 1124

Electron Emission Current From Oxide Coated Cathode Subject To High Electric Field

By Chokichiro SHIBATA

Research Division, Nihon Musen,
Mitaka, Tokyo

(Received April 11, 1960)

In the process of experimental studies on the electron emission from oxide coated cathode subject to high electric field such as is encountered in high power magnetrons and klystrons, the author has found the fact that the relation between electron emission current and applied field differs from the well known "Schottky effect".

Test tubes were small gap diodes, in which the anode was made of tungsten rod 4 mm in diameter and the cathode consisted of a nickel disc 6 mm in

diameter, whose oxide coated area was 2 mm in diameter.

In the Schottky region, $\log i$ vs $\sqrt{E}$ curves should show straight lines¹⁾. In fact, it is seen, in fig. 1 (a), that the relation in the low field region where DC measurement was made, is in agreement with the Schottky effect, but in the high field region where pulsed measurement was made, deviation from the Schottky effect is observed.

Tube No. 1 had the cathode of 50μ oxide coating. Tube No. 2 was prepared as follows, by using tube No. 1 after completing all the measurements with it.

Tube No. 1 was injected with wet hydrogen gas and the cathode heated in that atmosphere, then the tube exhausted and treated in ordinary ways. After these processes, the No. 2 cathode is considered to be far less porous than the No. 1 cathode.

The dependency of $\log i/T^2$ upon $1/T$ is shown in fig. 1 (b). There have been several discussions about the anomalous emission from oxide coated cathode²⁾³⁾. One of those is that the anomalous emission is due to the local high field on the oxide surface. In that case, the dependency of $\log i/T^2$ upon $1/T$ must be a straight line. In fig. 1 (b), this relation appears correct only in the low field region.

The gradient of the Schottky line is given by

$$d \log i / d \sqrt{E} = e^{3/2} / kT$$

Measurements of the relation of $d \log i / d \sqrt{E}$ VS $1/T$ are shown by the curves in fig. 2. In DC measurements (low field) using both No. 1 and No. 2, and in pulse measurements (high field) using No. 2, the curves seem to be parallel to the theoretical line. But pulse emission from No. 1 cathode does not obey this relation.

From these measurements, it seems that in very high fields, such as of a few thousands volts per centimeter, the mechanism of the high emission current from oxide coated cathode differs from the mechanism of the so called "Schottky effect". As to this anomalous emissions, the author wishes to publish his own theoretical interpretation elsewhere, and presently only the measured results are reported in brief.

The author wishes to thank Prof. I. Takahashi, Prof. H. Kawamura and Prof. S. Mito for their discussions and the author's thanks are due to Dr. S. Fukagawa and Dr. Y. Yasuoka for their encouragements and also to Mr. Y. Araki for his assistance.

References

- 1) W. Schottky: Phys. z. s. **15** (1914) 872.
- 2) H. Y. Fan: J. Appl. Phys. **14** (1943) 552.
- 3) R. L. Sproull: Phys. Rev. **67** (1945) 166.

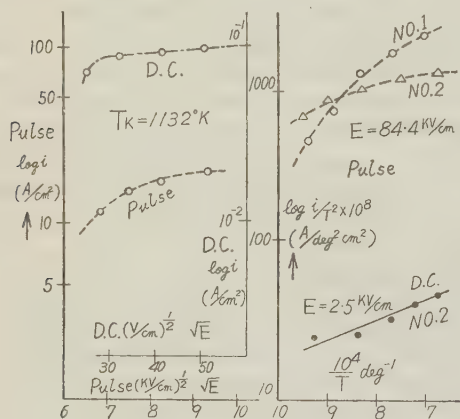


Fig. 1(a).

Fig. 2(b).

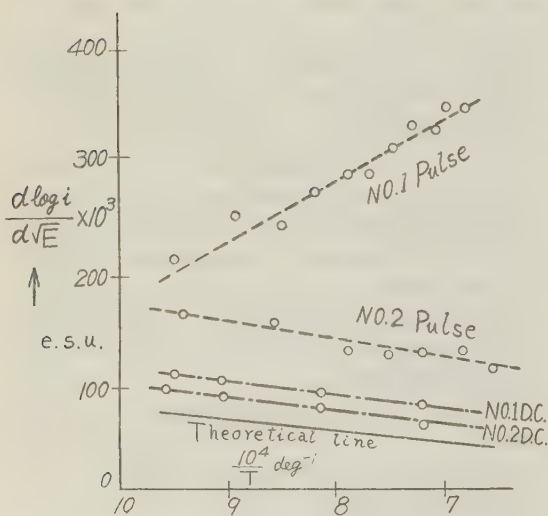


Fig. 2.

J. PHYS. SOC. JAPAN **15** (1960) 1125**Magnetic Hyperfine Structure of the 3, 2 Line of Ammonia**

By Koichi SHIMODA and Kunitaka KONDO

*Department of Physics, Faculty of Science,
University of Tokyo, Tokyo, Japan*

(Received April 14, 1960)

The magnetic hyperfine structure of the $J=3$, $K=2$ line of N^{14}H_3 was observed by a beam type maser spectrometer. Fairly complete investigations on the magnetic hyperfine structure in the inversion spectrum of ammonia have been carried out by several authors^{1), 2)}. However, the 3, 2 line exhibits an exceptional case, where the quadrupole interaction vanishes in the first order so that the spin of the nitrogen nucleus I_N is coupled to the rotational angular momentum J only by the weak magnetic interaction. This coupling competes with the magnetic interaction between the protons and the magnetic field due to molecular rotation. Then the coupling scheme which is used for other rotational states breaks down, and $F_1 = J + I_N$ is no longer a constant of motion for the 3, 2 state. Theoretical treatment for this case was given by Hadley³⁾, who calculated the magnetic hyperfine structure shown in Fig. 1.

The focuser, the beam source and the cavity are essentially the same as those reported before⁴⁾.

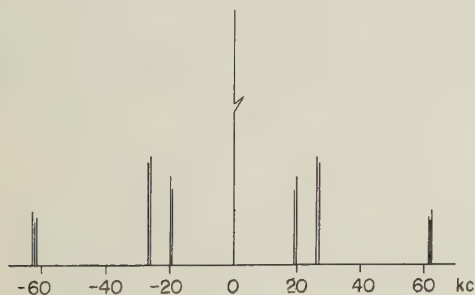
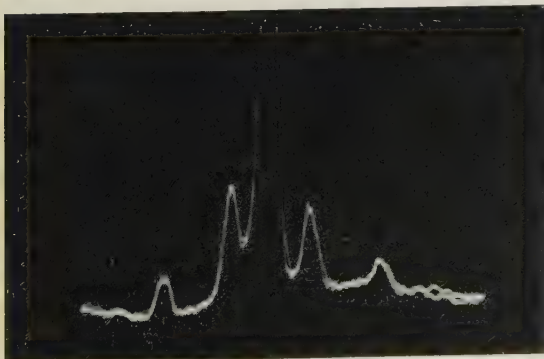
Fig. 1. Calculated spectrum of the 3, 2 line³⁾.

Fig. 2. Observed spectrum of the 3, 2 line.

The microwave power is supplied by a crystal doubler driven by a klystron X-13. The multiplied frequency f is converted into $f+45$ Mc and $f-45$ Mc by a crystal converter, so that one of these sideband frequencies may fit the frequency of the line at 22,834.18 Mc. The signal power emitted from the molecular beam is mixed with the carrier wave of frequency f to produce 45 Mc beat, which is amplified, rectified and displayed on an oscilloscope. A typical picture of the observed spectrum is shown in Fig. 2.

The frequency separation of magnetic hyperfine satellites and the half-width of the line were measured by using modulation sidebands of the central line which were generated by biasing the crystal doubler at a frequency variable from 2 to 70 kc.

If the electronic structure or the atomic distances for the upper and lower inversion states are not exactly the same, slight asymmetry in the hyperfine structure will appear. The observed separation appears to be symmetric about the main line within the accuracy of the present measurement. They are 62.59 ± 0.30 kc for the outer and 24.35 ± 0.15 kc for the inner satellites.

The inner satellites were observed as single lines with the typical half-width of 6.1 ± 0.2 kc. This is an apparent inconsistency with the theoretical spectrum in Fig. 1, which gives doublet structure for the inner satellites with the separation of 6.9 kc. The observed half-width of the main line and the inner satellites changes from 3.6 kc to more than 7 kc with the increase of signal power. Weak field Zeeman effect of the line was also measured. The outer satellites are considered to be somewhat broadened by the residual magnetic field of the order of 0.8 oersteds.

The complete analysis of the Zeeman effect as well as the hyperfine structure of the line is now in progress and will be reported in near future.

References

- 1) G. R. Gunther-Mohr, et al.: Phys. Rev. **94** (1954) 1184, 1191.
- 2) J. P. Gordon: Phys. Rev. **99** (1955) 1253.
- 3) G. F. Hadley: Phys. Rev. **108** (1957) 291.
- 4) K. Shimoda: Proc. Conference on Quantum Electronics, 1960, Columbia Univ. Press. and J. Phys. Soc. Japan **13** (1958) 939.

J. PHYS. SOC. JAPAN **15** (1960) 1126~1127

Some Observations on the Domain Walls in Thin Films

By Yasuo GONDŌ and Zenya FUNATOGAWA

Department of Physics, Yokohama National University, Yokohama

(Received March 16, 1960)

We have observed the colloidal patterns on 20% Fe-Ni films with uniaxial magnetic anisotropy. The films were evaporated on microscope cover glasses. The thickness of the films varied from 100Å to 4000Å and the substrate temperature was changed from the room temperature up to 300°C. The evaporation was performed in vacuum of 3×10^{-5} mmHg and the observations were done without annealing.

The character of walls observed on the films are shown in Fig. 1. In the thinner films (< 250 Å) the Néel type double walls^{(1), (2), (3)} occur and in the thicker films the Bloch type walls⁽¹⁾. The so-called cross-tie walls^{(4), (5)} are only observed in the intermediate thickness range (from about 250Å to 1000~2500Å). It is noted that the range is dependent on the substrate temperature remarkably. In the thicker films the walls become more straight and thin, and it is explained by the development of the Bloch type walls. The thicker the film thickness, the more difficult the colloidal observation of the Bloch type walls was.

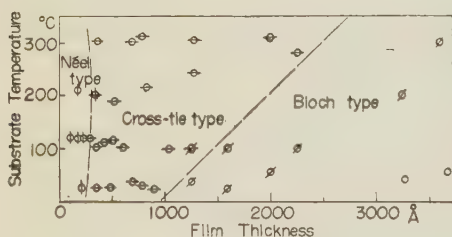


Fig. 1. Character of the domain walls observed on thin 20% Fe-Ni films. $\circ$: the Bloch type, $\odot$: the cross-tie type and $\oplus$: the Néel type.

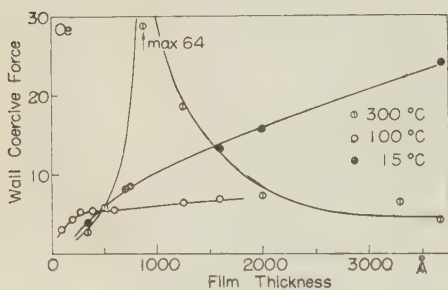


Fig. 2. Dependence of the wall coercive force on the film thickness and the substrate temperature.

An anomaly of the wall coercive force is found in a certain thickness range of the films evaporated at 300°C. It is shown in Fig. 2. The wall coercive force is affected by the wall energy and this anomaly is explained by an increase of the wall energy due to the magnetostatic energy of the wall in this thickness range^{(1), (2)}. Actually this range almost coincides with that of the cross-tie wall. However, the wall coercive force of the films evaporated at the room temperature has no anomaly. In these films large planar stresses are induced. In such cases, it is necessary that a contribution of the magnetoelastic energy to the wall energy is under consideration. Detailed discussions on the effect of the planar stress to the character of the wall and the wall coercive force will be reported in near future.

A confirmation of the model of the cross-tie walls proposed by Huber *et al.*⁽⁴⁾ is made by the application of a transverse magnetic field. In a demagnetized state stable cross-tie walls distinctly occur in the easy direction. Applying a weak field in the hard direction, a half of each section of the main wall disappears and the cross-ties begin to curve. Finally the cross-tie wall turns into a sort of line of arrows ($\rightarrow \rightarrow$). Reversing the weak field, the direction of the arrow is reversed reversibly ($\leftarrow \leftarrow$) (Fig. 3). It is suggested that

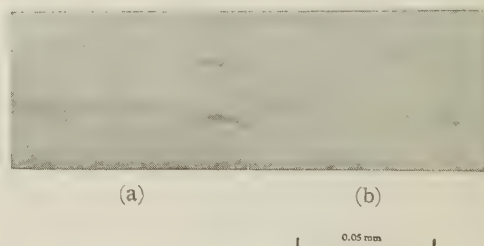


Fig. 3. The cross-tie walls observed in a 400 Å 20 Fe-Ni film. A weak transverse field is applied in the film plane and perpendicular to the wall. (a) 1.5 Oe upward, and (b) 2 Oe downward.

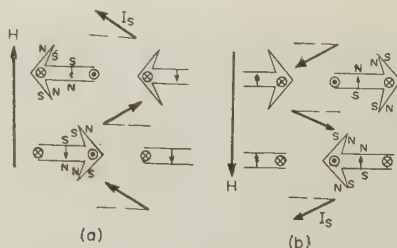


Fig. 4. Suggested interpretation of the observations in Fig. 3. The relation between rotation of the magnetization and the polarity of the wall in the film plane is shown. $\odot$: I vertically out of plane, $\otimes$: I vertically into plane.

this behavior is due to the reversible rotation of magnetization in domains and walls without wall displacement. A suggested interpretation of the observations, which is standing on the same model as the previous⁴⁾ assuming the polarity reversal between neighbouring sections of the main wall and also between opposite halves of the wall of each cross-tie, is shown in Fig. 4.

It is a pleasure to acknowledge a part of the measurements by H. Koyama and H. Konno. The present work was partly supported by the Scientific Research Grant from the Ministry of Education.

References

- 1) L. Néel: Comt. rend. **241** (1955) 533.
- 2) L. Néel: J. phys. radium **17** (1956) 2250.
- 3) H. J. Williams and R. C. Sherwood: J. Appl. Phys. **28** (1957) 548.
- 4) E. E. Huber, Jr., D. O. Smith and J. B. Godenough: J. Appl. Phys. **29** (1958) 294.
- 5) R. M. Moon: J. Appl. Phys. **30** S (1959) 84.

J. PHYS. SOC. JAPAN **15** (1960) 1127

On the Possibility of Ferromagnetism for an Electron Gas

By Masao SHIMIZU

Department of Physics, Tokyo Metropolitan University, Tokyo

(Received April 4, 1960)

The conclusion that an electron gas does not show ferromagnetism at all electron densities because of the effect of the correlation was given by Wigner¹⁾ and Pines²⁾ respectively. They compared the energy of an electron gas when all the spins of electrons are parallel with that when the electron gas is in a normal non-magnetic state by their respective methods and obtained the above conclusion.

At first sight it may be imagined that if an electron has a heavier effective mass the electron gas would be ferromagnetic, but this is not necessarily so. Although this fact has already been described in the previous paper³⁾, in this short note we would like to give a more definite proof to this point.

We compare the energy of the electron gas at the ferromagnetic state with that at the normal state. The electron gas has the Hamiltonian, $H = - \sum_i (\hbar^2/2m^*)p_i^2 + \sum_{i < j} e^2/r_{ij}$, where m^* is an effective mass and is supposed to be larger than the ordinary electron mass m , that is, $\lambda = m^*/m > 1$. If we replace the effective mass m^* and the electron coordinates r in H by λm and r'/λ respectively, we have $H = \lambda \{ - \sum_i (\hbar^2/2m)p_i'^2 + \sum_{i < j} e^2/r_{ij}' \}$, where $r_{ij}' = |r_i' - r_j'| = \lambda r_{ij}$. This Hamiltonian is nothing

but λ times larger than the ordinary Hamiltonian, although all the electron coordinates are elongated by λ .

Since the energy of the electron gas with the ordinary Hamiltonian, in which $m^*/m = \lambda = 1$, when all electron spins are parallel cannot become lowest at all electron densities, we can conclude that also in the electron gas with the Hamiltonian H , in which $m^*/m = \lambda > 1$, the energy for the state in which all the spins are parallel cannot become lowest at all electron densities and at all values of λ .

As pointed out by Wigner, state with intermediate moments should also be considered. Making use of the Bohm-Pines collective description of electron interaction⁴⁾ and the assumption that the screening distance is independent of magnetization, and including the short-range correlation energy due to the second-order perturbation-calculation of the screened Coulomb interaction, we have calculated the total energy of the electron gas with $\lambda = 1$ as a function of the total spin magnetic moment of the electron gas and found that the energies at all electron densities increase monotonously with increasing magnetic moments⁵⁾.

Then as a conclusion it is most probable that the electron gas is not ferromagnetic at all densities and at all effective masses, unless the electron gas becomes unstable as a gaseous aggregate^{1, 6)}.

On the other hand, if the periodic lattice potential is taken into account for the electron gas, we can expect that the electron gas becomes ferromagnetic at certain conditions as shown in the previous paper by using the simple model³⁾.

Anyhow, the periodic lattice potential is important in explaining the ferromagnetism of transition metals by the itinerant electron gas model, because the effect of the correlation prevents an electron gas from being ferromagnetic and the spin-wave motion in the electron gas model will be unstable because of the correlation if we disregard the effect of the lattice potential.

I wish to express my sincere thanks to Prof. R. Kubo for giving me an opportunity to stay at Research Institute of Fundamental Physics, Kyoto University, and Prof. T. Matsubara, Drs. Y. Kitano, A. Yoshimori and T. Izuyama for valuable discussions at Research Institute of Fundamental Physics.

References

- 1) E. P. Wigner: Trans. Faraday Soc. **34** (1938) 678.
- 2) D. Pines: Phys. Rev. **92** (1953) 626.
- 3) M. Shimizu: J. Phys. Soc. Japan **15** (1960) 376.
- 4) D. Pines: *Solid State Physics*, vol. I (Academic Press Inc., New York, 1955) 367.
- 5) Details will be published elsewhere.
- 6) M. Shimizu: J. Phys. Soc. Japan **15** (1960) 217.

J. PHYS. SOC. JAPAN **15** (1960) 1128~1129

Structure of Giant Resonance in
 $\text{Al}^{27}(p, \gamma)$ Reaction

By Motoharu KIMURA, Katsufusa SHODA,
Naoshi MUTSURO, Tsutomu TOHEI,
Kazuo SATO, Kunishige KURODA,

Department of Physics, Faculty of Science,
Tohoku University, Sendai, Japan

Katumi KURIYAMA and Tosimitu AKIBA

Department of Physics, Faculty of Science,
Tokyo University of Education, Otuka,
Bunkyo-ku, Tokyo, Japan

(Received March 26, 1960)

Measurements of 90° yield of gamma rays resulting from the capture of protons, with energies from 7.5 to 14.7 MeV in Al^{27} have been made using the INS (University of Tokyo) variable energy cyclotron¹⁾. Gamma rays leading to the ground state of Si^{28} ($Q=11.58$ MeV) which will be referred to hereafter as γ_0 , and those leading to the first excited state (1.78 MeV), γ_1 , were measured using $4''\phi \times 4''\text{NaI(Tl)}$ detector with enough shields. The two gammas could not be separated from each other. The target was an aluminum foil with purity of 99.6% and of 9μ in thickness. Proton beams of $0.3\text{--}0.5\mu\text{A}$ were passed through the foil with glancing angle of 45° and lead to the beam catcher. Fig. 1 is an example of the gamma ray spectrum which also shows the background spectrum without target. Fig. 2 is the relative cross section curve for $\text{Al}^{27}(p, \gamma_0 + \gamma_1)\text{Si}^{28}$ as a function of proton energy. This reveals a full structure of

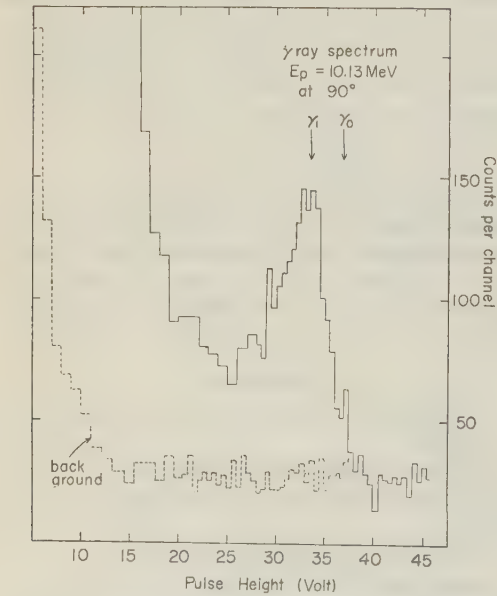


Fig. 1. Example of the gamma ray spectrum and the background spectrum without target.

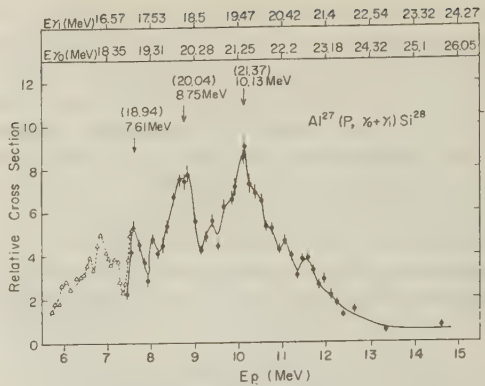


Fig. 2. Relative cross section curve for $\text{Al}^{27}(p, \gamma_0 + \gamma_1)\text{Si}^{28}$ as a function of proton energy.

giant resonance if combined with results of Canberra²⁾. The width of giant resonance is of the order of 4 MeV with many resonance peaks and also possibly with giant resonance splitting due to deformation.

At least three resonances at 7.61 MeV, 8.75 MeV and 10.13 MeV of laboratory proton energy can be attributed to the excited level of Si^{28} . Gove et al.³⁾, using tandem Van de Graaff, also found many resonances. If we neglect the sharp rise and down of resonances, it looks very plausible that the main part of giant resonance is split into two peaks. According to the theory of Okamoto and Danos⁴⁾, this means the spheroidal deformation of compound nucleus. If so, the eccentricity $e=(R_1-R_2)/R_0$ of Si^{28} nucleus becomes about 0.05 with possible prolate sign. This is very reasonable if we consider the deformation of Al^{27} and Si^{29} to be +0.15 and -0.15 respectively according to Bromley et al.⁵⁾. The absolute cross section of $\text{Al}^{27}(p, \gamma_0 + \gamma_1)\text{Si}^{28}$ assuming isotropic emission of gammas at the proton energy of 10.13 MeV is about $160\mu\text{-barn}$ with estimated error of $\pm 20\%$. This is the peak value and is too small if extrapolated from the Canberra results. Expected cross section estimated from the $\text{Si}^{28}(\gamma, p)$ process using detailed balance is about one order of magnitude larger than the above value. This is not unreasonable, however, if we consider the energy distribution of emitted protons in (γ, p) process. Detailed description will be published later.

We wish to acknowledge very stimulating and helpful discussions with Dr. K. Okamoto who is now at Tohoku University. We also express sincere thanks to the cyclotron crew of the INS, University of Tokyo, for their help in cyclotron operation and other arrangements.

References

- 1) S. Kikuchi, et al.: Institute for Nuclear Study, University of Tokyo, J. Phys. Soc. Japan **15** (1960) 41.

- 2) D. S. Gemmel, A. H. Morton and L. B. Smith: Nucl. Phys. **10** (1959) 33. D. S. Gemmel, A. H. Morton and E. W. Titterton: Nucl. Phys. **10** (1959) 45.
- 3) H. E. Gove, A. E. Litherland and R. Batchelor: Phys. Rev. Letters **3** (1959) 177, and also private communication from K. Okamoto.
- 4) K. Okamoto: Prog. Theor. Phys. Japan **15** (1956) 75; Phys. Rev. **110** (1958) 143. M. Danos: Nucl. Phys. **5** (1958) 23.
- 5) D. A. Bromley, H. E. Gove, E. B. Paul, A. E. Litherland and E. Almquist: Canad. J. Phys. **35** (1957) 1042, 1057.

J. PHYS. SOC. JAPAN **15** (1960) 1129

The Behaviours of Free Radicals Trapped in γ -Irradiated Polyethylene

By Hisatsugu KASHIWABARA*)

and

Kenichi SHINOHARA

Tokyo Laboratory, Japanese Association for Radiation Research on Polymers, Kamifujima-cho, Bunkyo-ku, Tokyo

(Received March 17, 1960)

The behaviours of free radicals produced in γ -irradiated polyethylene were investigated by means of electron spin resonance (ESR).

The samples used were high-density Marlex 50 (HD) and low-density Sumikathene (LD), which were irradiated by γ -radiation of Co-60 in vacuum and at room temperature. The measurements were made at a frequency of 9400 Mc/sec under the same conditions as that of irradiation.

A resonance spectrum of HD irradiated with dose of 3×10^7 rads consists of five lines which are difficult to resolve (Fig. 1a). The resonance spectra of HD and LD are almost the same in shape and spreading. Detailed discussions on the spectra, however, will be given in a forthcoming paper.

The yields of free radicals *vs* irradiation dose for HD and LD are shown in Fig. 1b. The number of radicals produced is in the order of 2 spins per 10,000 carbons for HD irradiated in dose of 3×10^7 rads. The initial rates of free radical productions per 100 eV of energy absorbed (G-value) are 0.5 and 0.3 for HD and LD, respectively. The ratio of the yields in HD and LD is proportional to the ratio of the degrees of crystallinity in respective samples. Hence it is considered that the free radicals which are detectable in ESR measurements at room temperature are the ones trapped in crystalline regions of the samples.

If the polyethylene crystallite is assumed to be composed of *n*-paraffine chains¹⁾, C_nH_{2n+2} , the part

* On leave from Fuji Spinning Company.

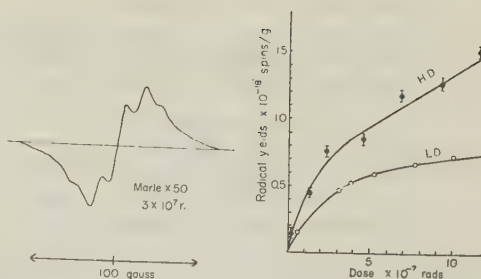


Fig. 1a.

Fig. 1b.

Fig. 1a. ESR spectrum of irradiated Marlex 50 (First Derivative curve). Fig. 1b. Radical yields *vs* irradiation dose in vac. and room temp.

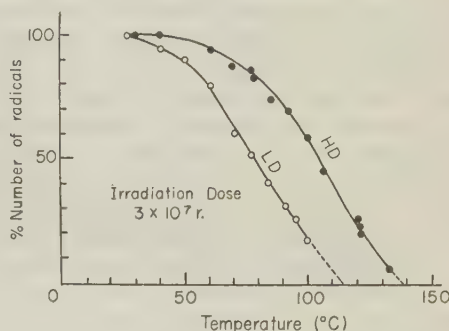


Fig. 2. Number of radicals *vs* temperature of post-irradiation heating for 2 min.

of crystalline portions which melts at a given temperature is a portion of *n*-paraffine chains, melting point of which is below the same temperature. Fig. 2 shows the number of free radicals *vs* temperature of post-irradiation heating; after irradiation, samples were kept in a bath of each temperature until thermal equilibrium is reached, then absorption intensities due to free radicals remaining were measured. The number of free radicals which vanish at various temperature ranges will be proportional to the density of *n*-paraffine in the crystallite which are to melt at the same temperature ranges; i.e., the crystal size distribution as a function of *n* may be obtained. With LD, more than 90% of the initial radicals vanish below 105°C which is the melting point of $C_{70}H_{142}$. With HD, half of the radicals yet remain above the same temperature. Therefore, it is considered that the larger crystallites exist in HD than in LD. Since the curves tend to the melting points of respective samples, it is considered that the crystal destruction may be not apparent in the case of γ -irradiation in the range of dose of this study (3×10^7 rads).

Reference

- 1) A. Charlesby and L. Callaghan: Phys. Chem. Solids **4** (1958) 306.

Temperature Dependence of Tunnel Diode Characteristics

By Yoshitaka FURUKAWA

*The Electrical Communication Laboratory,
Musashinoshi, Tokyo*

(Received March 25, 1960)

The qualitative features¹⁾ of the characteristics of tunnel diodes may be accounted for by writing the junction current as

$$z \int \{f_o(E) - f_v(E)\} \rho_o(E) \rho_v(E) dE$$

where z is the tunneling probability, and f 's are the Fermi functions. Both z and the integral in above expression contribute to the temperature dependence of the maximum current $I_{\max}$, in the forward direction. The integral increases and begins to saturate with decreasing temperature, and the more the degeneracy of electrons is, the faster the saturation occurs. On the other hand, z is given by $\exp \{-cE_g(1/n+1/p)^{1/2}\}$, where c is a constant and $E_g(T)=E_g(0)-\beta T$ is the energy gap at $T^\circ\text{K}$. z decreases with decreasing temperature, becomes insensitive to T for high carrier concentrations. Therefore, it may be expected that $I_{\max}$ has positive temperature coefficient at low temperatures, and the higher the carrier concentration is, the less the temperature dependence becomes.

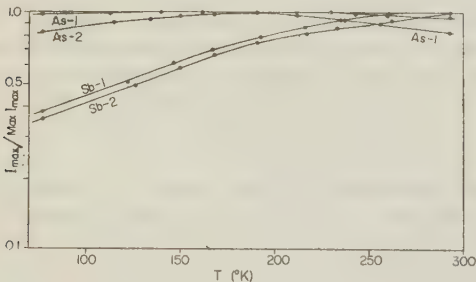


Fig. 1. $I_{\max}$ versus T curves.

Tunnel diodes have been made of As- or Sb-doped germanium. Fig. 1 shows the temperature dependence of $I_{\max}$. In this figure, $I_{\max}$ is normalized for its maximum value in measured temperature range ($77^\circ\text{K}\sim 293^\circ\text{K}$). Expected results have been obtained.

For sample Sb-2, $d/dT \cdot \log I_{\max}$ is equal to $6.85 \times 10^{-3} (T^{-1})$ at low temperatures, and $(1/n+1/p)^{1/2}$ of this sample is $4.7 \times 10^{-10} (\text{cm}^3)^{1/2}$. cE_g at 293°K has been determined experimentally²⁾ and is 2.72×10^{10} for Sb-doped germanium. Therefore, β , the temperature coefficient of energy gap, is given by

$$\beta = \frac{6.85 \times 10^{-3} E_g(293^\circ\text{K})}{2.72 \times 10^{10} (1/n+1/p)^{1/2}} = 3.7 \times 10^{-4} (\text{eV}/^\circ\text{K})$$

Table I.

Specimen	Impurity	N (cm^{-3})	$I_{\max}$ at 293°K
As-1	As	2.5×10^{19}	35.8 mA
As-2	As	6.1×10^{18}	$64.0 \mu\text{A}$
Sb-1	Sb	6.0×10^{18}	$18.4 \mu\text{A}$
Sb-2	Sb	4.9×10^{18}	$6.18 \mu\text{A}$

from the present experiment. This value is in good agreement with the value obtained from other experiments.³⁾

However, an appreciable difference between As- and Sb-doped samples has been observed. For the same electron concentration, diodes made of Sb-doped germanium show positive temperature dependence even at room temperature, while diodes made of As-doped germanium show negative temperature dependence at this temperature. It is believed, tentatively, that this difference relates with the degeneracy of conduction band,^{2),4),5)} The conduction band of As-doped germanium is deformed by heavy doping, and the state density or the effective mass is increased, but this is not the case for Sb-doped germanium. The increase of effective mass results in the decrease of degeneracy temperature for a given carrier concentration. This explains the observed result. This hypothesis can also explain the difference⁶⁾ of temperature dependence of electron mobility in As- and Sb-doped germanium.

The author thanks Mr. Z. Kiyasu, the associated director and Dr. T. Niimi heartly for the encouragement in the course of this work. He is also indebted to Mr. T. Takahashi for preparation of heavily doped crystals.

References

- 1) L. Esaki: Phys. Rev. **109** (1958) 603.
- 2) Y. Furukawa: Phys. Soc. Japan **15** (1960) 730.
- 3) G. G. Macfarlane et al.: Phys. Rev. **108** (1957) 1377.
- 4) N. Holonyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, H. Ehrenreich: Phys. Rev. Letter **3** (1959) 167.
- 5) J. L. Pankov: Phys. Rev. Letter **4** (1960) 20.
- 6) Y. Furukawa: unpublished.

J. PHYS. SOC. JAPAN **15** (1960) 1131~1132**Paramagnetic Resonance of Mn^{++} - F^- Pair in Sodium Chloride**

By Yasaburo YOKOZAWA

*Research Institute of Applied Electricity,
Hokkaido University, Sapporo*

(Received March 10, 1960)

Paramagnetic resonance of Mn^{++} - F^- pair in the single crystal of sodium chloride was observed.* Crystals were grown by the Kyropoulos method from a melt into which about 0.001 mole fraction of MnF_2 has been added. The sample was attached to the bottom of a reflection cavity working at room temperature and in 10 kMc/sec region and an external magnetic field was rotated in the (001) plane of the crystal.

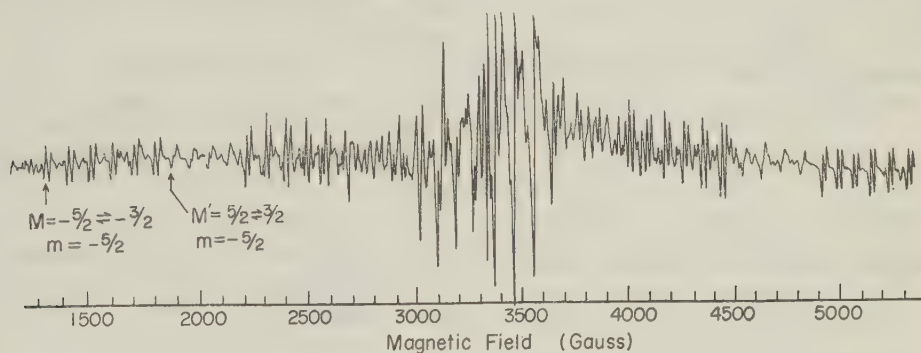


Fig. 1. The spectrum of Mn^{++} - F^- in NaCl. The magnetic field is parallel to the cubic axis of the crystal. M and M' designate the magnetic quantum number of Mn^{++} ; M corresponds to Mn^{++} those Mn^{++} - F^- direction is parallel to H and M' perpendicular to H .

principal axes of the hyperfine tensor which agrees almost with the cubic axes of the crystal, and I^F is the fluorine nuclear spin and A^F the hyperfine interaction tensor between the manganese electronic spin and the fluorine nuclear spin. The shift due to this interaction is calculated by Tinkham²⁾ and it is

$$\Delta H = A_s I_s + A_p I_s (3 \cos^2 \theta - 1),$$

where θ is the angle between the external magnetic field and the σ -bonding axis of Mn^{++} - F^- .

The spin Hamiltonian constants are given in Table I. Since the axes 2 and 3 are equivalent, the both signs of E are available. The moderately large value of E suggests the existence of a vacancy located in the next nearest neighbor cation

* The resonance of Mn^{++} - O^{--} in NaCl which was observed by Watkins¹⁾ as a weak absorption overlapped on that of the host crystal, was also observed in some crystal used in the present study. In this experiment, it was fairly strong and not overlapped on the resonance of the host crystal.

Complex structures were observed in a "not-quenched" crystal. The spectrum which is observed when a magnetic field is parallel to [100] direction is shown in Fig. 1. The doublet structures of each hfs of Mn^{++} show the existence of Mn^{++} - F^- pair in the crystal. According as the direction of the magnetic field deviates from [100] direction, these complex structures become obscured, except the case when the magnetic field directs to [110]. This is because the Mn^{++} - F^- direction makes small angle with the cubic axis of the crystal and the energy levels of Mn^{++} mix complicately with each other. These spectra are described by the spin Hamiltonian

$$\mathcal{H} = g\beta H \cdot S + DS_1^2 + E(S_2^2 - S_3^2) + AS \cdot I + I^F \cdot A^F \cdot S,$$

where 1, 2 and 3 indicate the directions of the

Table I. Spin Hamiltonian constants of Mn^{++} - F^- in NaCl.

g	1.9988 $\pm$ 0.0004	
D	-449.9 $\pm$ 1.0	gauss
E	$\pm$ 69.9 $\pm$ 1.0	gauss
A	-89.2 $\pm$ 1.0	gauss
$ A_s $	15.2 $\pm$ 0.5	gauss
$ A_p $	2.9 $\pm$ 0.5	gauss

site of Mn^{++} and perpendicular to Mn^{++} - F^- direction. As for the super-hyperfine constants A_s and A_p , they are nearly equal to those of $Mn^{++}(F^-)_6$ that are observed by Hayes *et al.*³⁾ for Mn^{++} in NaF or other crystals.²⁾⁻⁵⁾

From the value of A_s , one can estimate that a σ -bond of Mn^{++} - F^- pair has 0.45% $2s$ character, while Watkins¹⁾ estimated that there is 3.3% $3s$ character per one bond in a σ -bond of $Mn^{++}(Cl^-)_6$ in sodium chloride. By subtracting the contribution of the direct dipole-dipole interaction, 0.6 gauss, from A_p , it may be concluded that $2p\sigma$

character is about 2.4% at fluorine nucleus. The contribution is calculated standing on a point-charge model and assuming the same separation of $Mn^{++}-F^-$ distance to that of Na^+-Cl^- in sodium chloride.

Weak absorptions were overlapped upon the above mentioned spectrum, but the analysis were not possible.

The author wishes to thank Mr. S. Ogawa for the valuable discussions and Mr. Y. Kazumata for the preparation of crystals and the assistance of the measurement.

References

- 1) G. D. Watkins: Phys. Rev. **113** (1959) 79.
- 2) M. Tinkham: Proc. Roy. Soc. A, **236** (1956) 535, 549.
- 3) W. Hayes and D. A. Jones: Proc. Phys. Soc. London **71** (1958) 503.
- 4) J. M. Baker, B. Bleaney and W. Hayes: Proc. Roy. Soc. A, **257** (1958) 141.
- 5) S. Ogawa and Y. Yokozawa: J. Phys. Soc. Japan **14** (1959) 1116.

J. PHYS. SOC. JAPAN **15** (1960) 1132~1133

Inverse Solution of the Thomas-Fermi Equation

By Louis Gold

*Project Matterhorn, Princeton University,
Princeton, New Jersey*

(Received July 23, 1958)

(Revised manuscript received January 18, 1960)

The computational tables for the Thomas-Fermi (TF) function have been incomplete in the sense that an inverse function has been lacking. Thus if it is desired to find an untabulated radial position, corresponding to a specified potential, interpolation may be required; or successive approximations may have to be carried out to attain the desired degree of accuracy.

The present communication provides the inverse TF series solution with expressions for the first eight coefficients. It turns out that these coefficients become increasingly laborious to evaluate and that the series is rapidly convergent in the neighborhood of the atomic nucleus where the reduced potential $\phi \rightarrow 1$. Unfortunately, the inverse series is not generally better adapted for the tabulation of TF functions. It may, therefore, find rather limited application—at least in its present form.

It may be inferred that heretofore the inverse solution defied description since the reversion approach conventionally employed for this purpose does not lend itself to a formal attack. The present

note concerns the derivation of the inverse TF series directly from the appropriate differential equation by a method first described for the characterization of inverse Bessel functions¹⁾.

For the ordinary TF equation

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \quad (1)$$

it is well known²⁾ that the solution for smaller values of x may be expressed as a series having the form

$$\phi = 1 + a_2x + a_3x^{3/2} + a_4x^2 + a_5x^{5/2} + \dots \quad (2)$$

were the customary statistical atom boundary conditions

$$\phi(0) = 1, \quad \phi'(0) = \text{const} \equiv a_2 \quad (3)$$

preclude the possibility of a closed-form solution. The a_i coefficients are merely numerical coefficients or functions of a_2 , a_2 itself being chosen to represent certain physical situations; in the instance of the free neutral atom³⁾

$$a_2 = -1.58807102.$$

Now an inverse solution intrinsically of the form $x = \phi(\phi)$ may be posed as $x = f(\phi)$ where it is convenient to define $\phi = 1 - \phi$. Thus an indicial equation

$$x = f(\phi) = b_1\phi^v + b_2\phi^{v+p} + b_3\phi^{v+2p} + \dots \quad (4)$$

must be employed in the inverse differential equation to prescribe v and p . The inverse of Eq. (1) can be shown¹ to be

$$f, \phi^v [f'' \phi^v]^2 - (1 - \phi^v) [f' \phi^v]^6 = 0 \quad (5)$$

with the concomitant findings

Table I: The b_i Coefficients for the Inverse TF Function

b_1	$-1/a_2$
b_2	$4/3b_1^{5/2}$
b_3	$8/3b_1^4$
b_4	$(2/45)b_1^{5/2}(140b_1^3 - 9)$
b_5	$(1/405)b_1^4(6400b_1^3 - 729)$
b_6	$(1/1890)b_1^{5/2}(80,080b_1^6 - 12,852b_1^3 + 81)$
b_7	$(1/17,010)b_1^4(2,007,040b_1^6 - 413,280b_1^3 + 9396)$
b_8	$(1/4,592,700)b_1^{5/2}(1,551,950,400b_1^9 - 389,188,800b_1^6 + 16,249,896b_1^3 - 18,225)$

Table II: Numerical b_i for the Free Neutral Atom ($a_2 = -1.58807102$)

b_i	Numerical Value
b_1	.6296947601
b_2	.4195308818
b_3	.4192654250
b_4	.3629742276
b_5	.3373440088
b_6	.3103877877
b_7	.2895808212
b_8	.2719917768

$$\left. \frac{d\phi}{dx} \right|_{x=0} = \frac{1}{b_1} = - \left. \frac{d\phi}{dx} \right|_{x=0} = -a_2 \quad (6)$$

$$v=1, \quad p=1/2$$

Further details of the analysis are outlined in the Appendix whereby the b_i coefficients are evaluated (see Table I). Numerical computations have been performed for the indicated a_2 value associated with the free neutral atom. The so-determined values of b_i are listed in Table II.

The author is greatly indebted to Miss Virginia Johnson of the MIT Lincoln Laboratory for aid

during the earlier stages of the calculations, and to Mrs. Joan Peskin of the Matterhorn Computer Group for painstaking review and finalizing of the manuscript.

Appendix: Development of b_i Coefficients

The ansatz for $f(\psi)$ given by equation (4) into the inverse differential equation (5), after some manipulation, leads to relations delineating the b_i . Thus equating the coefficients of the indicated terms below to zero provides the expressions

$$\begin{aligned} \psi^0 : \quad & \frac{9}{16} b_1 b_2^2 - b_1^6 = 0 \\ \psi^{1/2} : \quad & 3b_1 b_2 b_3 + \frac{9}{16} b_2^3 - 9b_1^5 b_2 = 0 \\ \psi : \quad & b_1 \left(4b_3^2 + \frac{45}{8} b_2 b_4 \right) + \frac{57}{16} b_2^2 b_3 - \frac{135}{4} b_1^4 b_2^2 - 12b_1^5 b_3 + 3b_1^6 = 0 \\ \psi^{3/2} : \quad & 3b_1 (3b_2 b_3 + 5b_3 b_4) + 7b_2 b_3^2 + \frac{99}{16} b_2^2 b_4 - \left(15b_1^5 b_4 + 90b_1^4 b_2 b_3 + \frac{135}{2} b_1^3 b_2^3 \right) + 27b_1^5 b_2 = 0 \\ \psi^2 : \quad & \frac{225}{16} b_1 b_4^2 + 24b_1 b_3 b_5 + \frac{105}{8} b_1 b_2 b_6 + \frac{189}{8} b_2 b_3 b_4 + \frac{153}{16} b_2^2 b_5 + 4b_3^3 - 18b_1^5 b_5 - \frac{225}{2} b_1^4 b_2 b_4 \\ & - 60b_1^4 b_3^2 - 270b_1^3 b_2^2 b_3 - \frac{1215}{16} b_1^2 b_2^4 + 36b_1^5 b_3 + \frac{405}{4} b_1^4 b_2^2 - 3b_1^6 = 0 \\ \psi^{5/2} : \quad & 45b_1 b_4 b_5 + 35b_1 b_3 b_6 + 18b_1 b_2 b_7 + \frac{315}{16} b_2 b_4^2 + 36b_2 b_3 b_5 + \frac{219}{16} b_2^2 b_6 + 19b_3^2 b_4 - 135b_1^4 b_2 b_5 - 21b_1^5 b_6 \\ & - 150b_1^4 b_3 b_4 - \frac{675}{2} b_1^3 b_2^2 b_4 - 360b_1^3 b_2 b_3^2 - 405b_1^2 b_2^3 b_3 - \frac{729}{16} b_1 b_2^5 + 45b_1^5 b_4 + 270b_1^4 b_2 b_3 \\ & + \frac{405}{2} b_1^3 b_2^3 - 27b_1^5 b_2 \\ \psi^3 : \quad & \frac{525}{8} b_1 b_4 b_6 + 36b_1 b_5^2 + 48b_1 b_3 b_7 + \frac{189}{8} b_1 b_2 b_8 + \frac{477}{8} b_2 b_4 b_5 + \frac{409}{8} b_2 b_3 b_6 + \frac{297}{16} b_2^2 b_7 \\ & + \frac{465}{16} b_3 b_4^2 + 28b_3^2 b_5 - 24b_1^5 b_7 - \frac{315}{2} b_1^4 b_2 b_6 - 180b_1^4 b_3 b_5 - 405b_1^3 b_2^2 b_5 - \frac{375}{4} b_1^4 b_4^2 \\ & - 900b_1^3 b_2 b_3 b_4 - 160b_1^3 b_3^3 - \frac{2025}{4} b_1^2 b_2^3 b_4 - 810b_1^2 b_2^2 b_3^2 - \frac{1215}{4} b_1 b_2^4 b_3 - \frac{729}{64} b_2^6 + 54b_1^5 b_5 \\ & + \frac{675}{2} b_1^4 b_2 b_4 + 180b_1^4 b_3^2 + 810b_1^3 b_2^2 b_3 + \frac{3645}{16} b_1^2 b_2^4 - 36b_1^5 b_3 - \frac{405}{4} b_1^4 b_2^2 + b_1^6 \end{aligned}$$

It is evidenced, then, that calculation of b_i beyond b_8 becomes prohibitive. The solutions for $b_2, b_3, \dots, b_8$ in terms of b_1 are compiled in Table I.

References

- 1) L. Gold: J. Math. and Phys. **36** (1957) 167.
- 2) See, for example, N. H. March: Proc. Phys. Soc. London A, **68** (1955) 726. R. P. Feynman,

N. Metropolis and E. Teller: Phys. Rev. **75** (1949) 1561. S. Kobayashi, T. Matsukuma, S. Nagai and K. Umeda: J. Phys. Soc. Japan **10** (1955) 759.

- 3) R. Latter: J. Chem. Phys. **24** (1956) 280.

J. PHYS. SOC. JAPAN **15** (1960) 1134~1135

A Simple Model of Aqueous Solution of Strong Electrolyte

By Takeshi SATOH

Department of Physics, Defense Academy,
Obaradai, Yokosuka

(Received March 4, 1960)

Bockris¹⁾ has suggested that the term hydration should be generally divided into two, primary and secondary sheaths. This suggestion corresponds to a structural interpretation presented by Frank and Wen²⁾. They consider the structure modifications in which an ion is surrounded by three concentric regions—the innermost one of immobilization of water molecules, the second one of structure breaking, and the third one of structurally normal water. Of course, we could not fix the boundaries between the region of structure breaking and that of normal water. Accordingly we admit that there remains some degree of unavoidable ambiguity in the definition of the secondary hydration region. On the basis of this background the author should like to offer a model of 1-1 electrolyte aqueous solution to be used throughout the whole concentration range.

It is convenient to introduce necessary quantities. Let the primary hydration number surrounded by each cation and anion be designated as $n_I^{(+)}$, $n_I^{(-)}$ and the average values of secondary hydration number surrounded by each cation and anion as $n_{II}^{(+)}$, $n_{II}^{(-)}$ respectively. Besides, we accept the assumption that dissociation into ions is almost complete even in concentrated range.

Let us consider the system in every state corresponding to varying concentration. In dilute range average distance between any pair of ions is fairly large, whilst it will decrease gradually with increasing of concentration. At last we come to a step where normal water can scarcely exist. On the way to this critical range secondary hydra-

tion number $n_{II}^{(+)}$ or $n_{II}^{(-)}$ will, of course, change complicatedly, particularly the more considerable the nearer to the critical range.

But here we assume that we can neglect such change occurred in hydration numbers. After concentration continues further, it will be possible to notice that a solution in such a concentrated range is different from that in a dilute range. It is clear that water molecules are in extraordinary state; in other words the system might be regarded to be an ionic solution dissolved in apparently different solvent.

Its characteristic nature might consist in quasi ionic lattice something like that of molten salts. These features are sketched in Fig. 1.

As evidence of our model we can quote several experimental data including molecular refraction and chemical shift of proton in nuclear magnetic resonance. Here we will pick up an example of dielectric relaxation. Hasted et al.³⁾ have shown that, as for an example of NaCl solution, relaxation wave length λ_s changes linearly to concentration c up to 1.5 mole/lit. But we assert that this linearity should be also valid with a different slope in concentrated range. Fig. 2 reproduces the result itself obtained by them. We would like to point out that the characteristic value λ_{s*} of water in structure-broken state can be determined as 15.9 cm by extrapolation from concentrated range. It is shorter than that of normal water by about 10%.

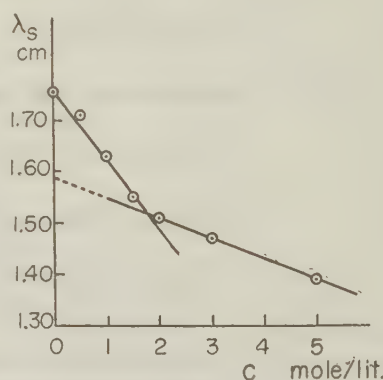


Fig. 2. Plot of relaxation wavelength λ_s of NaCl solution versus concentration c .

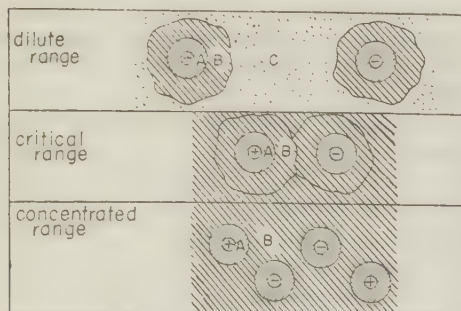


Fig. 1. A schematic explanation of model for electrolytic aqueous solution. A, primary hydration region; B, secondary hydration region; C, region of structurally normal water.

In a case of molecular refraction we can also find similar circumstances, characteristic molecular refraction R_* of water in structure-broken state being determined likewise. If we adopt conventional relationship that polarizability is proportional to molecular refraction, polarizability α_* corresponding to uncommon water molecule can be obtained. As for KBr solution its value is $1.426 \text{ \AA}^3$, which is smaller compared with the value $1.468 \text{ \AA}^3$ of normal water.

We can also estimate reasonable over-all second-

any hydration number, $n_{\Pi^{(+)}}+n_{\Pi^{(-)}}$. A fuller account giving the details of these analysis is being prepared for submission to elsewhere.

A kernal of our model is considered to consist in the existence of critical concentration which can be estimated to locate in almost 1.5~2.0 mole/lit.

References

1) J. O'M. Bockris: Quart. Rev. Chem. Soc., London **3** (1949) 173.
2) H. S. Frank and Wen-Yang Wen: Discuss. Faraday Soc. **24** (1957) 133.
3) J. B. Hasted: D. M. Ritson and C. H. Collie: J. Chem. Phys. **16** (1948) 1.

J. PHYS. SOC. JAPAN **15** (1960) 1135~1136

Correction to the Paper "Two-dimensional Flow of an Ideal Gas with Small Electric Conductivity past a Thin Profile "

By Takeo SAKURAI

Department of Aeronautical Engineering,
Faculty of Engineering,
Kyoto University

(Received March 28, 1960)

Recently, the author published a paper on the two-dimensional flow of an ideal gas with small electric conductivity past a thin profile. Soon after the publication of the paper, the author received a kind letter from Mr. S. Ando. He suggested in the letter that the forward wake in the subsonic case (Fig. 2*) will appear in the direction

$$\theta=\pi+a'\delta \qquad a'=\frac{2}{\sqrt{1-M_0^2}}$$

contrary to the author's previous result

$$\theta=\pi+a\delta \qquad a=\frac{2}{\sqrt{1-M_0^2}}\{1\pm M_0\sqrt{1-M_0^2}\} \qquad (49)$$

He also pointed out that the results in the supersonic case have an extra factor $1/\sqrt{2}$, in the limit of the ordinary gasdynamical case. The author reexamined the previous results and found out some errors, which are corrected in this note.

First, the forward wake in the subsonic case will appear in the direction

$$\theta=\pi+a'\delta \qquad a'=\frac{2}{\sqrt{1-M_0^2}} \qquad (49')$$

as Ando pointed out. (Fig. 2') This is readily shown if one minimizes the expression in the parenthesis of Eq. (48), in which all the terms of order δ^2 should be neglected. The procedure is

* The equations and the figures corresponding to those in the previous paper are distinguished by primes in this note.

consistent with the approximation applied to deduce Eqs. (39) and (40).

Secondly, the extra factor $1/\sqrt{2}$ is found to come from erroneous application of Riemann's method of integration in the previous paper. As is well known, the boundary curve of the region of integration must not cross a characteristic curve more than once. The boundary curve in Fig. 3 clearly violates the condition. The region in which Riemann's method of integration is performed must, therefore, be corrected as shown in Fig. 3'. Eq. (69) must, also, be corrected as follows

$$\begin{aligned} \phi(\xi_p, \eta_p) = & \frac{\phi(A) + \phi(B)}{2} \\ & + \frac{1}{2} \int_B^A \phi_\eta I_0 \left(\frac{L}{2} \sqrt{(\xi_p - \xi)^2 - \eta_p^2} \right) d\xi \\ & - \frac{L}{4} \int_B^A \frac{\eta_p}{\sqrt{(\xi_p - \xi)^2 - \eta_p^2}} \phi I_1 \left(\frac{L}{2} \sqrt{(\xi_p - \xi)^2 - \eta_p^2} \right) d\xi \end{aligned} \qquad (69')$$

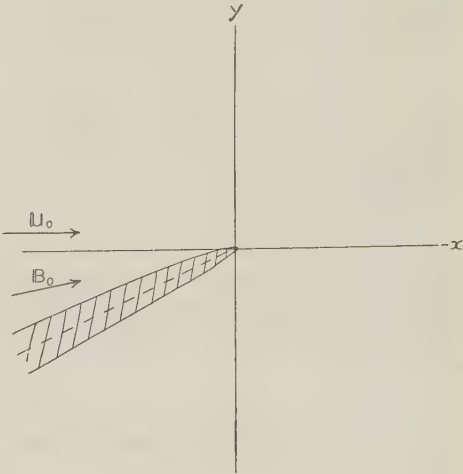


Fig. 2'.

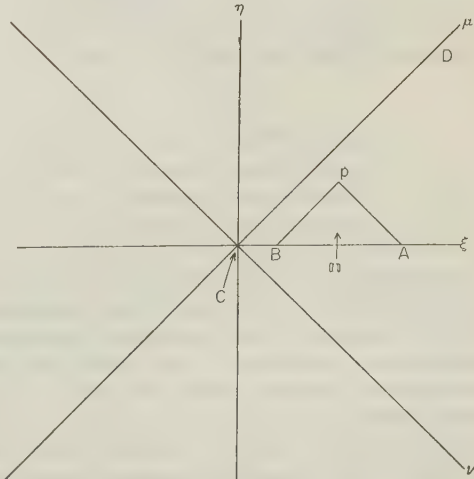


Fig. 3'.

where the extra factors $1/\sqrt{2}$ disappear because of the fact that the length scale in the (μ, ν) -plane is just $\sqrt{2}$ times as large as that of the (ξ, η) -plane and cancels out the extra factors. In the above, ϕ_η will be eliminated by use of the boundary condition on the surface of the profile (Eq. (72)), and the velocity potential on the profile is determined by the boundary condition $\phi=0$ on the characteristic curve CD emanating from the leading edge of the profile:

$$\phi(P)|_{\eta=0}=-\int_0^\xi \phi_\eta \, d\xi$$

where only the quantities of the lowest orders with respect to L , K and $K\delta$ are retained. The remaining procedure of determining the velocity potential, the velocity distribution over the profile and so on are similar to those in the previous paper. Thus we have the results:

$$\left. \begin{aligned} \phi_0 &= -\frac{1}{\sqrt{M_0^2-1}} \int_{-1}^{\xi_p} e^{K\xi/2} f_B'(\xi) \, d\xi \\ \phi_1 &= -\int_{-1}^{\xi_p} \phi_0 \, d\xi \end{aligned} \right\} \quad (74')$$

$$u=-\frac{f_B'(\xi)}{\sqrt{M_0^2-1}}-\frac{Kf_B(\xi)}{2\sqrt{M_0^2-1}}\pm K\delta f_B(\xi) \quad (75')$$

$$\left. \begin{aligned} C_D &= \frac{2t^2}{\sqrt{M_0^2-1}} \int_{-1}^1 (f_B')^2 \, d\xi \\ C_L &= -2tK\delta \int_{-1}^1 f_B \, d\xi \end{aligned} \right\} \quad (76')$$

Concluding the note, the author wishes to express his cordial thanks to Mr. Sigenori Ando for his kind information of the faults in the author's previous paper.

Reference

- 1) T. Sakurai: J. Phys. Soc. Japan **15** (1960) 326.

J. PHYS. SOC. JAPAN **15** (1960) 1136~1137

The Magnetic Properties of Mn-Sn-C Alloys

By Mitsuru ASANUMA

Department of Physics, Faculty of Science,
University of Hokkaido

(Received February 18, 1960)

It is known that the sign of exchange interaction of manganese atoms in various alloys of manganese can be both positive and negative. The sign is believed to be controlled by the mutual distance of manganese atoms and also by the kinds of intervening atoms.

Guillaud¹⁾ has discussed the magnetic interaction of a number of manganese compounds, i.e. Mn_2Sb , Mn_2As , Mn_4N , $MnBi$, etc., and suggested that the

lower limit of the distance between manganese atoms which will give a positive exchange interaction is about 2.81 Å.

$Mn_4C^{2)}$ and $Mn_4M^{3)}$ have been known as the magnetic manganese compounds with a simple crystal structure. Although Mn_4C is stable only at high temperatures, the double carbides of manganese and one of the elements of IIB, IIIB, and IVB in the periodic table have the same crystal structure as Mn_4C and Mn_4N , i.e., perovskite type structure, and are stable even at lower temperatures⁴⁾. In this case, the lattice parameter can be controlled by the addition of different amount of the elements of IIB, IIIB, and IVB. In view of this consideration, a number of compounds of Mn-Sn-C series was studied.

The specimens were prepared by heating the mixture of manganese, tin and graphite in a evacuated silica tube at 1100°C for a day and then annealing it at 900°C for two days. The experimental results are shown in the Table and Figs. 1 and 2.

Table				
Composition	Lattice Parameter	Mn-Mn distance	Magnetization/mol	Curie temp.
$Mn_{3.15}Sn_{0.85}C$	3.967Å	2.805Å	1.90 μ_B	385°K
$Mn_{3.25}Sn_{0.75}C$	3.961Å	2.800Å	1.80 μ_B	434°K
$Mn_{3.32}Sn_{0.68}C$	3.955Å	2.796Å	1.75 μ_B	520°K
$Mn_{3.49}Sn_{0.60}C$	3.947Å	2.791Å	1.70 μ_B	570°K
$Mn_{3.50}Sn_{0.50}C$	3.941Å	2.786Å	1.65 μ_B	592°K

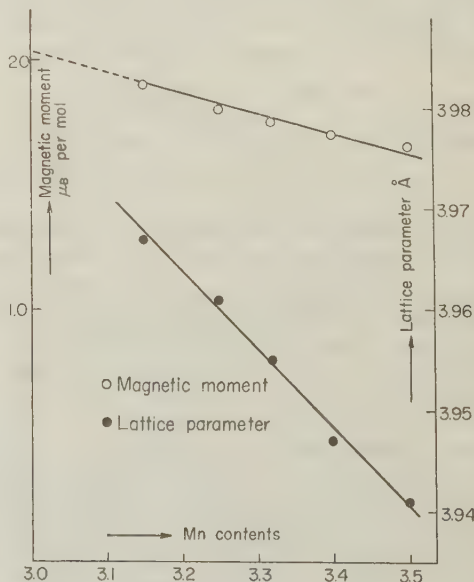


Fig. 1. The dependence of saturation magnetization and lattice parameter on manganese contents.

Butters and Myers⁵⁾ have suggested from the X-ray experiment that in the composition $Mn_{3+x}X_{1-x}C$, three manganese atoms occupy the face-centered positions, and the excess x manganese atoms occupy the positions of the cube corners of the pervskite unit cell. Here X is metalloid element.

The relation of magnetization to composition suggests that the magnetic momont of manganese atom at the cube corner should be antiparallel to that at the face-centered position, the value of magnetic moment per manganese atom at cube corner should be $0.85\mu_B$ which is estimated by the gradient of the curve in Fig. 1, and that at face-centered position should be $0.7\mu_B$, which is obtained by extrapolating the curve in Fig. 1 to the composition of Mn_3SnC . The Curie temperature increases with the decrease of lattice parameter as shown in the table, and this fact means that the coupling of magnetic moment increases with the decreases of Mn-Mn distance.

In order to ensure the ferrimagnetic behavior of crystal, it is necessary to measure the magnetic susceptibility above the Curie temperature. The dependence of the inverse of magnetic susceptibility per mol of $Mn_{3.15}Sn_{0.85}C$ on temperature is concave against the temperature axis as shown in Fig. 2 (a).

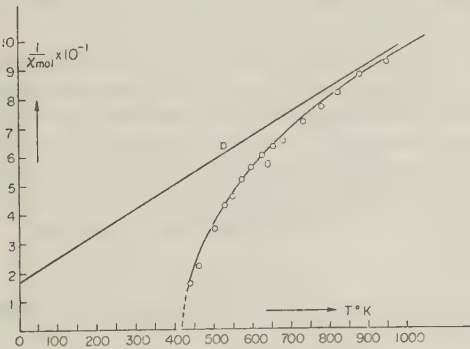


Fig. 2. The dependence of the inverse of magnetic susceptibility per mol on temperature.

When the experimental result is analysed by Néel's equations⁶⁾, the asymptote of experimental curve is obtained as in Fig. 2 (b), and the Curie constant and the asymptotic Curie point are estimated as $C_{mol} = 11.0$, $\theta = -121$. From the Curie constant C_{mol} , the effective Bohr magneton per manganese atom P_{eff} is calculated as $P_{eff} = 2.97$. Assuming the quenching of the orbital magnetic moment, this value corresponds to $S = 2.1/2$ on the average in crystal, and does not agree with the spin value expected from the measurement of saturation magnetization. This discrepancy is not explained at present.

References

1) C. Guillaud: Rev. Mod. Phys. **25** (1953) 119.

2) E. R. Morgan: J. Metals A.I.M.M.E. **6** (1954) 98.
3) G. W. Weiner and J. A. Berger: J. Metals A.I.M.M.E. **7** (1955) 360.
4) W. B. Pearson: *A Handbook of Lattice Spacing and Structures of Metals* (Pergamon Press, New York, 1956).
5) R. G. Butters and H. P. Myers: Phil. Mag. **46** (1955) 132.
6) L. Néel: Ann. physique **3** (1948) 137.

J. PHYS. SOC. JAPAN **15** (1960) 1137~1138

Conductivity Induced by Injected Electrons in Liquid Dielectrics

By Pyong-un CHONG, Tomihiko SUGIMOTO and Yoshio INUISHI

Department of Electrical Engineering, College of Engineering, Osaka University
(Received April 1, 1960)

In the electric conduction and breakdown in liquid dielectrics drift mobility and ionization by collision may play an important rôle. Recently H. LeBlanc has reported on the "electron" drift mobility¹⁾ in n-Hexane at lower electric fields. We have been investigating on the behaviours of electrons and ions in liquid dielectrics at higher electric fields. Here some of our results on drift mobility measurement in n-Hexane and Benzene will be mentioned.

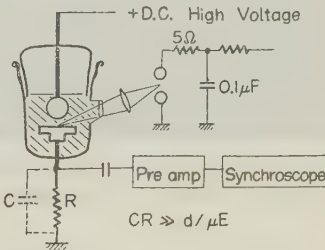


Fig. 1. Experimental arrangement.

The experimental methods, as shown in Fig. 1, were almost similar to those adopted in the investigations of gaseous discharges²⁾. Light pulse of about 4μ sec duration, which was generated by discharging the air gap, injects photoelectrons into liquid dielectrics from the magnesium cathode. These initial electrons induce electric current under D.C. field application by drifting towards the anode as free electrons or as negative ions. For the experimental convenience, charging method was adopted for induced current observation.

Fig. 2 (a) shows a typical wave form of induced

charge signal on input stray capacitance by photo-induced current in *n*-Hexane. The slope of charge signal was constant upto the saturation value under a given D.C. field and electrode separation. This fact shows that the injected electrons or negative ions have a constant velocity across the gap. From thus obtained transit time, denoted by τ in Fig. 2 (a), we can calculate the drift mobility of negative charge carriers in pure *n*-Hexane, which was about $0.85 \times 10^{-3} \text{ cm}^2/\text{volts sec}$ as shown in Fig. 3. It should be noticed that the drift mobility does not depend on the applied electric field nor gap distance in this range of the experiments. By adding 1% Ethyl Alcohol to *n*-Hexane somewhat different charge signal was observed. As shown in Fig. 2 (b), the charge signal, in this case did not show such a sharp knee as in pure *n*-Hexane and the transit time was about two times longer than in

pure *n*-Hexane at the same condition. In Benzene the value of the drift mobility obtained by the same procedure was about $0.42 \times 10^{-3} \text{ cm}^2/\text{volts sec}$ independent of the field and gap distance.

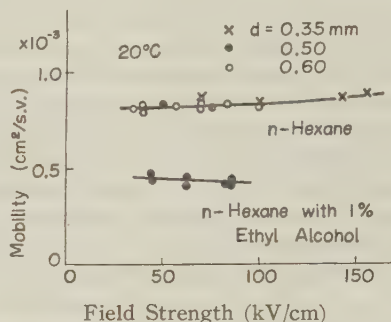


Fig. 3. Drift mobility in *n*-Hexane and *n*-Hexane with 1% Ethyl Alcohol.

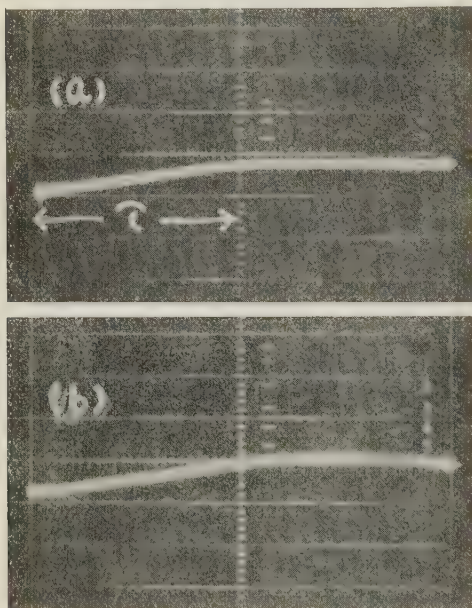


Fig. 2. Induced charge signals in (a) *n*-Hexane and (b) *n*-Hexane with 1% Ethyl Alcohol.

At this stage of the experiments whether the drift mobility obtained here is that of electrons as was suggested by H. LeBlanc¹⁾ or that of negative ions³⁾ can not be determined conclusively. Judging from the order of the mobility and the magnitudes of the viscosity of *n*-Hexane (3.04×10^{-3} poise) and Benzene (6.00×10^{-3} poise), it is not so unreasonable to take it as that of negative ions formed by electron attachments.

We are now proceeding our experiments at higher electric fields upto breakdown and trying to find the field dependency of the drift mobility of injected electrons and the existence of charge multiplication in liquid dielectrics. The authors wish to express their sincere thanks to Professor T. Suita for his guidance and encouragements.

References

- 1) O. H. LeBlanc, Jr.: J. Chem. Phys. **30** (1959) 1443.
- 2) J. A. Hornbeck: Phys. Rev. **80** (1950) 297.
- 3) S. Satō, S. Nagao and Y. Toriyama: Brit. J. Appl. Phys. **7** (1956) 297.

Errata

Magnetic Hyperfine Spectrum of H₂CO by a Maser

By Hiroshi TAKUMA, Tadao SHIMIZU and Koichi SHIMODA

J. Phys. Soc. Japan **14** (1959) 1595

Page	Column	Line	
1596		Eq. (4)	$H = \sum [\dots] + \dots$ should read $H = - \sum [\dots] + \dots$
		7	$b(= \dots$ should read $b = \dots$
		3 from the bottom	term should read part.
1597		1	term should read part.
		Eq. (5)	$H = \sum_{K=1,2} \sum_{g=x,y,z} A_{Kg} \bar{I}_{Kg} J_g - \dots$ should read $H = - \sum_{K=1,2} \sum_{g=x,y,z} A_{Kg} \bar{I}_{Kg} J_g + \dots$
			$\left[\frac{1}{2} J(J+1) - \dots \right]$ should read $\left[\frac{1}{3} J(J+1) - \dots \right]$
		Eqs. (7 and 8)	$H = \sum \dots$ should read $H = - \sum \dots$
		Eq. (4)	Eq. (4) should read Eq. (9).
		1 to 3 from the bottom	These equations should be denoted as Eq. (10).
		Eqs. (9 and 10)	The sign of the right hand side should be reversed.
1598	Left	Fig. 3	The sign of the co-ordinate should be reversed.
1599	Left	12	Fig. 4 should read Fig. 3.
		13, 15 and 16	$\Delta v_2 - \Delta v_4$ should read $\Delta v_4 - \Delta v_2$, and $\Delta v_4 - \Delta v_3$ should read $\Delta v_3 - \Delta v_4$.
		21	$\Delta v_{J+1} = -\frac{\Delta X}{2(J+1)} + \frac{\Delta Y}{2(J+1)(J+3)}$ should read $\Delta v_{J+1} = \frac{\Delta X}{2(J+1)} - \frac{\Delta Y}{2(J+1)(2J+3)}$
		22	$\Delta v_J = \frac{\Delta X}{2J(J+1)} + \dots$ should read $\Delta v_J = -\frac{\Delta X}{2J(J+1)} + \dots$
		23	$\Delta v_{J-1} = \frac{\Delta X}{2J} - \dots$ should read $\Delta v_{J-1} = -\frac{\Delta X}{2J} - \dots$
		14 from the bottom	$\langle J_y^2 \rangle = \frac{1}{2} J(J+1) - K - C_1$ should read $\langle J_y^2 \rangle = \frac{1}{2} \{ J(J+1) - K - C_1 \}.$
Right	11	$\Delta v_1 - \Delta v_3$	should read $\Delta v_3 - \Delta v_1$.
	12	$\Delta v_3 - \Delta v_2$	should read $\Delta v_2 - \Delta v_3$.

Angular Dependencies of Efficiencies for Sodium-Iodide Crystals

By Tadayoshi DOKE, Atsushi NAKAMOTO, Yasukiyo TAKAMI,
Manabu HATTORI and Shinji OKANO

J. Phys. Soc. Japan **15** (1960) 737-738

The authors' name "Shinji OKANO" should be read "Masaharu OKANO".

Errata

Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO

By Kazuko MOTIZUKI

J. Phys. Soc. Japan **15** (1960) 888

In the paper titled as above the author took wrong relative signs for the two types of the hyperfine field in Co^{++} , one the hyperfine field arising from the residual orbital moment and spin dipole moment, $H_l + H_a$, and the other the Fermi type hyperfine field, H_F . The former should be parallel to the magnetic moment of the ion, i.e., antiparallel to the angular momentum vector (spin and orbital), whereas the author took the reverse. The latter is antiparallel to the magnetic moment of the ion. Therefore, these two fields subtract each other instead of that they add. Since all the calculations given in this paper refer to the plus spin sub-lattice, the sign of $H_l + H_a$ has to be reversed. The frequency of the central line comes out to be 490 Mc, instead of 1028 Mc as given by Eq. (2.14). Further, the calculated line width becomes 0.017 Mc, instead of 0.115 Mc. Other modifications are as follows:

Sign should be reversed in the right-hand sides of (2.7), (2.8), (2.10), (3.5), and the first three lines of (4.9).

In the right-hand side of (2.12), 10.29 should be read -4.91.

(2.14) should be $\nu_0 = 490$ Mc.

6th line from the bottom on p. 893, left, is read

-10.13 Mc, -0.0255 Mc, and +0.0020 Mc, re-

2nd line from the bottom on p. 893, left, is read

which is +0.0704 Mc, etc.

On p. 895, correct numerical values are:

$$\alpha_{n,n.} = +3.689 \times 10^{-6} \times \dots$$

$$\alpha_{n,n.n.} = +6.969 \times 10^{-6} \times \dots$$

$$\alpha_{n,n.} = +.0.25 \text{ oe}, \quad \alpha_{n,n.n.} = +1.48 \text{ oe}$$

$$\sqrt{\langle (\hbar A \omega)^2 \rangle_{av}} = 8.53 \text{ oe}$$

$$8.53 \times 2 = 17.06 \text{ oe} \quad \text{or} \quad 0.017 \text{ Mc} \quad (\text{below (5.11)})$$

There are typographical errors:

p. 891, (3.4): $\alpha^2 k_Q'''$ instead of $\alpha^2 k_Q$

p. 893, top line, middle: $\times 10^{-8}$ instead of $\times 10^{-2}$

p. 894, (5.1): ϕ_{mk} instead of ϕ_{mk}

p. 895, (5.5), after the second double summation: $\frac{1}{2}$ is to be eliminated

Contents

(Vol. 15)

No. 1

Page

Radiations from Ba ¹⁴¹	Kunio NAGATANI	1
Angular Correlation Measurements in the Decay of In ^{114m}	Mitsuhiro KAWAMURA	3
Elastic Scattering of 14 Mev Protons by Deuterons and by Protons.....	Seishi KIKUCHI, Junpei SANADA, Shigeki SUWA, Izuo HAYASHI, Keigo NISIMURA and Kiyoji FUKUNAGA	9
Investigation of the Reaction Mg ²⁶ (p, γ)Al ²⁶	Jiro MUTO	17
Gamma-rays from the Reaction Al ²⁷ (p, γ)Si ²⁸	Kotoyuki OKANO	28
A 160 cm Synchro- and Variable Energy Ordinary Cyclotron	Seishi KIKUCHI, Itaru NONAKA, Hiroshi IKEDA, Hiroo KUMAGAI, Yoshio SAJI, Junpei SANADA, Shigeki SUWA, Akira ISOYA, Izuo HAYASHI, Kazuhisa MATSUDA, Hisashi YAMAGUCHI, Takashi MIKUMO, Keigo NISIMURA, Takashi KARASAWA, Shinsaku KOBAYASHI, Ken KIKUCHI, Satoru ITO, Arata SUZUKI, Seiichiro TAKEUCHI and Hiroshi OGAWA	41
On the Variation Principle in the Kinetic Theory of Dense Gases, I.....	Terutosi MURAKAMI	60
Dislocation Model of Liquid Structure	Sanchi MIZUSHIMA	70
Approach to Equilibrium of A Large Fermion System	Kyoji NISHIKAWA	78
Annealing of γ-Ray Damage in Germanium	Tsunesaburo ASADA, Haruo SAITO, Kazumi OMURA, Taiji OKU and Masahiro OKA	93
A. C. and D. C. Field Effects on Cleaned Germanium Surfaces	Shinji KAWAJI	95
Crystal Structure of Silicon Carbide of 174 Layers	Takanori TOMITA	99
Electron Diffraction Study of Ice	Kohji SHIMAOKA	106
Theory of Electron-Oscillations in Non-Uniform Plasmas	Masao SUMI	120
Electroluminescence in Zinc Sulfide Single Crystals.....	Shin-ichiro NARITA	128
Electron Microscope Study of the Decomposition Process of Oxide Coated Cathods	Shoichi HIROTA and Tetsuji IMAI	137
Thermoluminescence of Zinc Sulfide Phosphors.....	Kikusaburo OSADA	145
A Refinement of the Linearized Transonic Flow Theory	Iwao HOSOKAWA	149
General Theory of Electrically Conducting Perfect Gas Flow past a Three-Dimensional Thin Body	Shigenori ANDO	157
Condenser Microphones with Plastic Diaphragms for Airborne Ultrasonics, II	Kiichiro MATSUZAWA	167
A Linearized Theory of Magnetohydrodynamic Flow past a Fixed Body in a Parallel Magnetic Field	Hirowo YOSINOBU	175
Magnetohydrodynamic Flow past a Sphere	Kanefusa GOTOH	189

SHORT NOTES

Effect of Charged Dislocation on the Thermoelectric Power of Semiconductors	Tokio OHTA	197
Influence of Foreign Magnetic Nuclei on NMR	Akira MIYAKE and Riichirô CHÛJÔ	198
Thermal Conductivity of KNO ₃	Ikushi YOSHIDA and Shozo SAWADA	199
On a Solution of the Paraxial Ray Equation in an Axially Symmetrical Electrostatic Field	Noboru SHIBATA	200
NMR Second Moment of a Radical Oscillating in a Periodic Potential	Riichirô CHÛJÔ	201
Temperature Dependence of T ₁ of Cl ³⁵ in Para-dichloro-benzene.....	Akira HIRAI	201
Synthesis of AlN Crystals	Tetsuo MATSUMURA and Yasaku TANABE	203
Crystal Growth of CdS in the Vertical Furnace..	Haruo FUJISAKI and Yasaku TANABE	204
Dislocations in Si Single Crystals	Takashi FURUOYA and Yozo SASAKI	205
Observation of Layer Structure in Dislocation Free Silicon Crystals with the Use of X-ray Anomalous Transmission.....	Zensho ISHII, Takashi FURUOYA, Yozo SASAKI and Kazutake KOHRA	206
Intervalley Scattering of Hot Electrons	Motoichi SHIBUYA and Wataru SASAKI	207
On the Quasi-two-dimensional Laminar Boundary Layer.....	Nisiki HAYASI	208

Magnetic Properties of $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$	Kiiti SIRATORI and Shuichi IIDA	210
Formation Mechanism of F-Centers in KCl Single Crystals Heated in Potassium Vapor	Hiroyuki MIZUNO and Morio INOUE	211

Errata

Relative Intensities of Zeeman Components in Nuclear Quadrupole Resonance Spectrum	Masaharu TOYAMA	196
--	-----------------	-----

No. 2

Three New Isotopes, Co^{63} , Ga^{76} and As^{81}	Haruhiko MORINAGA, Tokihiro KUROYANAGI, Hidehiko MITSUI and Katsufusa SHODA	213
On the Stability of an Electron Gas at Low Density	Masao SHIMIZU	217
Detection and Determination of Equilibrium Vacancy Concentrations in Aluminum	Soji NENNO and J. W. KAUFFMAN	220
Une Nouvelle Forme du Nitrure de Nickel: Ni_4N	Nobuzo TERA0	227
Crystal Texture of LiF Single Crystals by X-Ray Technique	Hiroshi NIMURA	231
The Theory of the Fine Structure of the X-ray Absorption Spectrum, II.	Toshio SHIRAIWA	240
Studies on the Magnetic Anisotropy Induced by Cold-Rolling of Ferromagnetic Crystal, II. Iron-Aluminum Alloys	Sōshin CHIKAZUMI, Kenzō SUZUKI and Hiroko IWATA	250
Dielectric Relaxation in High Polymers, II. Vinylic High Polymers	Tomoyasu TANAKA and Yōichi ISHIDA	261
Indirect Nuclear Spin-Spin Couplings in Saturated Hydrocarbon Molecules	Eiko HIROIKE	270
Potential Barrier of Phenol from its Microwave Spectrum	Takeshi KOJIMA	284
Zeeman Effect of Nuclear Quadrupole Resonance Spectrum in 1, 3, 5-Trichlorobenzene	Yonezo MORINO and Masaharu TOYAMA	288
Microwave Spectrum of Ethyl Iodide, I.	Takahiro KASUYA and Takeshi OKA	296
Microwave Zeeman Effect of Formaldehyde	Kunitaka KONDO, Hiromasa HIRAKAWA, Akira MIYAHARA, Takeshi OKA and Koichi SHIMODA	303
Stark-Zeeman Effects on Asymmetric Top Molecules. Formaldehyde H_2CO	Kunitaka KONDO and Takeshi OKA	307
Luminescences from KBr/KI Single Crystals	Masao TOMURA and Yōzo KAIFU	314
Flow of a Viscous, Electrically Conducting Fluid along a Circular Cylinder or a Flat Plate with Uniform Suction	Michiru YASUHARA	321
Two-dimensional Flow of an Ideal Gas with Small Electric Conductivity past a Thin Profile	Takeo SAKURAI	326
A New Type of Thermal Conductivity Gas Detector, I.	Shinzan SōMA and Yū TAKEUCHI	333
Non-ideality Effects upon the Sedimentation Equilibrium in a Density Gradient	Hiroshi FUJITA	336
Maxwell's Formula for Three-Dimensional and Large Deformation	Wataru SEGAWA	339
Ultrasonic Propagation through Aqueous Solutions of Acetates	M. KRISHNAMURTHI and M. SURYANARAYANA	345
Ultrasonic Propagation through Binary Mixtures containing Acetic Acid	M. KRISHNAMURTHI and M. SURYANARAYANA	349

SHORT NOTES

Photoconductivity in Nickel Doped Germanium	Yoshitaka FURUKAWA	353
Fluorine N.S.R. Spectroscopy, II. A "Distant" Carbon-13 Isotope Effect	George Van Dyke TIERS	354
Nuclear Quadrupole Resonance of Nitrogen in Cyanuryl Chloride	Shoji KOJIMA and Midori MINEMATSU	355
On the X-Ray Temperature Diffuse Scattering of Anthracene and Stearic Acid	Shoichi ANNAKA and J. L. AMORÓS	356
Photoconductivity of Cd-ZnS Mixed Crystals	Makoto KIKUCHI and Sigeru IIZIMA	357
Fine Structure in the $\text{N}^{14}(\gamma, n)\text{N}^{13}$ Activation Curve, II.		

..... Naoshi MUTSURO, Kazuo SATO and Masanori MISHINA	358
Thickness Dependence of Domain Orientation in Thin Nickel Films	
.....Kaizo KUWAHARA and Mitita GOTO	359
Magnetic and Electrical Anomalies of Iron Telluride Single Crystals	
..... Rokuroh NAYA, Miyuki MURAKAMI and Eiji HIRAHARA	360
Differential Cross Sections for the $N^{14}(d, p)N^{15}$ Ground State Reaction at the	
Deuteron Energy of 16 MeV	
Susumu MORITA, Nawoyuki KAWAI, Naoyuki TAKANO, Yorio GOTO,	
Reiko HANADA, Yutaka NAKAJIMA, Shigeo TAKEMOTO and Yûki YAEHASHI	361
A Curious Characteristic of P-N-P-N Junctions	
.....Takao KURATA and Kiichi KOMATSUBARA	362
Some Properties of X-ray damaged Rochelle Salt	Kenkichi OKADA 363
Lower Excited States in P^{29} Tatsuo TABATA, Hisao FUKUDA and Kotoyuki OKANO	364

Errata

Angular Distributions of Protons from the Reaction $^{12}C(\alpha, p)^{15}N$	
..... Itaru NONAKA, Hisashi YAMAGUCHI,	
Takashi MIKUMO, Iwao UMEDA, Tetsuo TABATA and Saburo HITAKA	365

No. 3

Energy Spectrum and Angular Distributions of Neutrons from the Reaction $Be^9(p, n)B^9$	
at 8 to 14 MeV of Proton Energies	Yoshio SAJI 367
Decay of Cl^{34m}	Tsutomu TÔHEI 372
Ferromagnetism of an Electron Gas	Masao SHIMIZU 376
Configurational Changes of Polypeptide Molecules in the Helix-Coil Transition	
Region, I.....	Kazuo NAGAI 407
Proton Magnetic Resonance and X-ray Diffraction Studies of Polypropylene	
.....Atsuo NISHIOKA,	
Yasuhiro KOIKE, Masakazu OWAKI, Tsunezo NARABA and Yoshinori KATO	416
On the Paramagnetic Inelastic Scattering of Neutrons due to Ions in the Anisotropic	
Crystalline Field	Yasusada YAMADA 429
Paramagnetic Resonance of Manganese in Alkali-Chlorides.....	Hisamitsu YOSHIMURA 435
On the Proton Resonance of Several Hexammine Complex Salts	Pil Hyon KIM 445
On the Magnetic Susceptibility of FeF_2	Akio HONMA 456
Volume Magnetostriction of Cobalt-Nickel Alloys	Takejiro KANEKO 463
Magnetic Anisotropy Measurements of MnO Single Crystal	
Enji UCHIDA, Hisamoto KONDOH, Yoshihide NAKAZUMI and Takeo NAGAMIYA	466
Effect of Solvent on the Extension of High Polymer Molecule	Hiroshi MIZUTANI 475
Paramagnetic Susceptibility of $CoCl_2 \cdot 6H_2O$ and its Deuterated Salts..	Taiichiro HASEDA 483
Photo- and Thermochemical Reactions in Potassium Chloride Crystals—A Quantita-	
tive Study of the M Centre.....	Tetsuhiko TOMIKI 488
On the Acoustic Radiation from a Flanged Circular Pipe	
.....Yûkichi NOMURA, Ichirô YAMAMURA and Sakari INAWASHIRO	510
Measures of Finite Strain and Stress-Strain Relations.....	Wataru SEGAWA 518
On Similar Solutions of the Steady Quasi-two-dimensional Incompressible Laminar	
Boundary-layer Equations.....	Nisiki HAYASI 522

SHORT NOTES

Heat Capacity of a Single Crystal of $MnCl_2 \cdot 4H_2O$	
.....H. FORSTAT, G. O. TAYLOR and B. R. KING	528
Purification of Alkali Halide Crystals through Fractional Distillation and Normal	
Freezing.....	Hiroshi KANZAKI and Keishiro KIDO 529
Ferrimagnetic Resonance in Polycrystalline Europium-Iron Garnet ($Eu_3Fe_5O_{12}$)	
..... Yûzô SHICHIJÔ, Tomonao MIYADAI and Hisao TAKATA	530
Microwave Discharge Chamber	Shûji FUKUI and Satio HAYAKAWA 531
Maser Oscillation on 6-6 Line of $N^{16}H_3$...Isao TAKAHASHI, Tsuneo HASHI, Masaru	
YAMANO, Motokazu YAMAMOTO, Shigeyoshi SUZUKI and Tsutomu MAKITA	532

Domain Patterns on Thin Films of Perminvar	
.....Yuzi GOMI, Yuzo ODANI and Makoto SUGIHARA	533
Jump Phenomenon in Resonance Curve of Ferroelectric Ceramics Katsuo NEGISHI	534
Chain Wall in Permalloy Thin Films Yuzi GOMI and Yuzo ODANI	535
Diffuse Scattering of X-ray by Gamma-ray Irradiated Rochelle Salt	
.....Koichi TOYODA, Akira SHIMADA and Tetsuro TANAKA	536
Influence of Preparation and Quenching on the Magnetic Properties of Precipitates in Cu-Co Alloy	
.....Masayoshi SATO and Tadayasu MITUI	537
Optical Bleaching of <i>R</i> -bands in LiF Crystals	
.....Kuniya FUKUDA, Akizo OKUDA and Yoichi UCHIDA	538

Errata

A 160 cm Synchro- and Variable Energy Ordinary Cyclotron Seishi KIKUCHI et al.	527
Electron Microscope Study of the Decomposition Process of Oxide Coated Cathods Shoichi HIROTA and Tetsuji IMAI	539

No. 4

Excitation Functions for Alpha-Induced Reactions on Manganese-55	
.....Shigeo TANAKA, Michiaki FURUKAWA, Takashi MIKUMO, Shiro IWATA, Masuo YAGI and Hiroshi AMANO	545
Differential Cross Sections for the Reaction $C^{12}(d, p)C^{13}$ in the Energy Range of Deuterons from 15- to 20-MeV	
.....Susumu MORITA, Nawoyuki KAWAI, Naoyuki TAKANO, Yorio GOTÔ, Reiko HANADA, Yutaka NAKAJIMA, Shigeo TAKEMOTO and Yûki YAEHASHI	550
Elastic and Inelastic Scattering of 11.2 MeV Deuterons	
.....Minoru TAKEDA	557
On the Phase Transition of Tungsten Trioxide below Room Temperature	
.....Sigetosi TANISAKI	566
Crystal Structure of Monoclinic Tungsten Trioxide at Room Temperature	
.....Sigetosi TANISAKI	573
Magnetic Properties of Iron Phosphide Fe_2P	
.....Shû CHIBA	581
Internal Friction of Quartz	
.....Yosio HIKI	586
Interaction of Exciton with Electron Trapping Centers in Alkali Halide Crystals. 2. Quantum Yield for the $U \rightarrow F$ Conversion and its Dependence on U - Center Concentration	
.....Masayasu UETA, Masamitsu HIRAI and Hiroyuki WATANABE	593
Multiple-Anode Proportional Counter X-Ray Diffractometer	
.....Jun-ichi CHIKAWA	602
The Quantitative Interpretation of Luminescent Properties of Cu-Activated Calcium Orthophosphate	
.....Yasuo UEHARA	612
Germanium Crystal as a Neutron Monochrometer and the Determination of its Higher Order Contaminations	
.....John T. WAJIMA, Brice M. RUSTAD and Edward MELKONIAN	630
Radiative Collisions between Molecular and Electron Beams, V. Angular Momentum Distributions of CH Separating from Simple Organic Molecules	
.....Tadao HORIE, Takayuki NAGURA and Masamoto OTSUKA	641
Microwave Spectrum of Cis-1, 2-Dichloroethylene	
.....Tadao SHIMIZU and Hiroshi TAKUMA	646
Theory of Solutions of Chain Molecules.....Hiroshi OKAMOTO	650
Theory of Electric Birefringence in Dilute Solutions of Tobacco Mosaic Virus.... Sekiko OGAWA and Syoten OKA	658
Notes on the Theory of Meissner Effect Masayuki ASAMI and Fumihiko TAKANO	669
Breakdown of Argon at Low Pressure in a Longitudinal Magnetic Field	
.....Kenji MITANI and Hiroshi KUBO	678
Ion-Electron Relaxation of Plasmas in a Magnetic Field, II.	
.....Taro KIHARA, Yukio MIDZUNO, Kyoko SAKUMA and Toshio SHIZUME	684
Axially Symmetric Stagnation-point Flow of an Electrically Conducting Fluid under Transverse Magnetic Field	
.....Tsunehiko KAKUTANI	688
Stokes Flow of an Electrically Conducting Fluid in a Uniform Magnetic Field Kanefusa GOTOH	696

An Investigation of Psychrometer, II.	Yoshirô OMORI	706
The Dynamic Bulk Viscosity of Polystyrene and Polymethyl Methacrylate	Ryusuke KONO	718

SHORT NOTES

Measurement of Piezoelectric Constants of a CdS Crystal	Toshio TANAKA and Shoji TANAKA	726
Electrical Conductivity of α -Fe ₂ O ₃	Tanehiro NAKAU	727
On the Proton Chemical Shift in Deuterium Substituted <i>p</i> -Xylene and Toluene	Hazime KUSUMOTO, Junkichi ITOH, Kozo HIROTA and Tomiko UEDA	728
Cold-emitting Cathode Materials	Yoshihiko MIZUSHIMA, Yoshitaka IGARASHI and Tetsuji IMAI	729
Tunneling Probability in Germanium <i>p</i> - <i>n</i> Junctions	Yoshitaka FURUKAWA	730
180° Domain Wall Motions in BaTiO ₃ Crystal.....	Kazuo HUSIMI	731
The Dislocation Etch Pits of CdS Crystals.....	Jiro NISHIMURA	732
Piezoresistivity in Semiconductive Barium Titanates	Osamu SABURI	733
Magnetic Susceptibility of CoBr ₂ ·6H ₂ O	M. GARBAR	734
Some Experiments on Plasma Alfvén Waves	Shigeo NAGAO and Teruyuki SATO	735
A Gamma Ray in Ti ⁴⁵ Decay	Chikai ISHII and Kasuke TAKAHASHI	736
Angular Dependencies of Efficiencies for Sodium-Iodide Crystals..Tadayoshi DOKE, Atsushi NAKAMOTO, Yasukiyo TAKAMI, Manabu HATTORI and Shinji OKANO		737

Errata

Volume Magnetostriction of Cobalt-Nickel Alloys	Takejiro KANEKO	738
Maxwell's Formula for Three-Dimensional and Large Deformation ..	Wataru SEGAWA	738

No. 5

The Reaction Li ⁷ (<i>p</i> , <i>n</i>)Be ⁷ , B ¹¹ (<i>p</i> , <i>n</i>)C ¹¹ and Al ²⁷ (<i>p</i> , <i>n</i>)Si ²⁷ at 8 to 14 MeV	Kazuo HISATAKE, Yoshihide ISHIZAKI, Akira ISOYA, Teruo NAKAMURA, Yoshihiro NAKANO, Bunsaburo SAHEKI, Yoshio SAJI and Kazunori YUASA	741
Protons from the <i>p</i> + <i>d</i> Breakup Reaction at Proton Energies of 14 MeV and 10 MeV	Seishi KIKUCHI, Junpei SANADA, Shigeki SUWA, Izuo HAYASHI, Keigo NISIMURA and Kiyoji FUKUNAGA	749
Measurements of the Polarization in Proton-Helium Elastic Scattering	Keigo NISIMURA Shigeki SUWA, Izuo HAYASHI, Kiyoji FUKUNAGA, Norio RYU and Masao SEKI	754
Elastic and Inelastic Scattering of Protons from N, Ne, Mg, Si, S and A in the Energy Range from 7.6 MeV to 14.2 MeV.....	Yukiyasu ODA, Minoru TAKEDA, Takashi YAMAZAKI, Chuin HU, Naoyuki TAKANO, Ken KIKUCHI, Shinsaku KOBAYASHI, Kazuhisa MATSUDA and Yukio NAGAHARA	760
Radial Distribution Function of Fluids, III.....	Kazuo HIROIKE	771
Expansion Theorem of Density Matrix, Virial Expansion and New Formula of Multiple Scattering	Toshio YOKOTA	779
Theoretical Study on the Properties of Coercive Field of BaTiO ₃ Single Crystal ..	Ryuji ABE	795
Heitler-London Approach to Electrical Conductivity and Application to <i>d</i> -Electron Conductions	Jiro YAMASHITA and Tatumi KUROSAWA	802
Anomalous Growth of MoO ₃ Crystals	Eiji YODA	821
The Change in Electron Mobility in Indium Antimonide at Low Electric Field	Yasuo KANAI	830
Visible Light Emission and Microplasma Phenomena in Silicon <i>p</i> - <i>n</i> Junction, I. ..	Makoto KIKUCHI and Kenkichi TACHIKAWA	835
A Possible Mode of Twin in the ϵ -phase of Cu-Sb Alloy	Michiyasu DOI	849
Shape of Nucleus Domain Anchored to a Screw Dislocation in Ferroelectric Crystal	Hidetosi TAKAHASHI, Terutaro NAKAMURA and Yoshihiro ISHIBASHI	853
Dynamical Theory of Electron Diffraction in Laue-case, II. Numerical Calculation of Intensities	Fuminori FUJIMOTO	859

The Effects of Deuteron Irradiation on the Nuclear Magnetic Resonance in Teflon	Hazime KUSUMOTO	867
On the Intramolecular Light Scattering of the Non-Gaussian Chain.....	Akira MIYAKE	875
Influence of the Molecular Weight Distribution on the Polymer Properties	Akira MIYAKE	883
Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO	Kazuko MOTIZUKI	888
Interaction between Rod-like Polyelectrolytes	Tsuyoshi OHNISHI, Nobuhisa IMAI and Fumio OOSAWA	896
Formation of Plasma by Low Energy Ion Injection and Cyclotron Heating	Tarô DODO	906
The Study of the Optical Properties of Conducting Tin Oxide Films and their Interpretation in Terms of a Tentative Band Scheme	Toshihiro ARAI	916

SHORT NOTES

Screened Impurity Potentials in Metals	E. C. McIRVINE	928
Magnetic Anisotropy Induced by Cold Rolling of Cu-Co Alloy	Tadayasu MITUI	929
On the Alpha-particles from the $\text{N}^{14}(d, \alpha)\text{C}^{12}$ Ground State Reaction..	Nawoyuki KAWAI	930
Ferromagnetism of Mn-Zn Alloy	Seiji TEZUKA, Sukeyoshi SAKAI and Yasuaki NAKAGAWA	931
Ferrimagnetism of Mn_5Ge_2 ...Kô YASUKÔCHI, Kazuo KANEMATSU and Tetuo OHYAMA		932
Spin Order in the Doublet at the Second Excited Level in Even-even Medium Nuclei	Mitsuo SAKAI	933
On the $F \rightarrow F'$ Conversion in the Presence of A-, M-, R-, and Z_1 -Centers.....	Hiroshi OHKURA, Katsunobu AWANE and Shigeko MIYAMOTO	934
Observation of Microplasma Pulses and Electroluminescence in Gallium Phosphide Single Crystal	Makoto KIKUCHI and Takashi IIZUKA	935
Magnetic Annealing of Co and Co-Ni Alloys...Minoru TAKAHASHI and Tatsuo KÔNO		936
Electrical Properties of Stannic Oxide Films.....	Isamu IMAI	937
Post-Irradiation Effect in Visible Absorption Spectra of Polyvinyl Chloride Sheets	Yoichi OKADA, Takao ITO and Ayao AMEMIYA	938
Interaction Effects in $\text{K}_3\text{Fe}(\text{CN})_6$	Taiichiro OHTSUKA	939
Temperature Dependence of Infrared Absorption Bands of n -Higher Alcohols.....	Mitugi HASIKUNI	941
Stress in Very Thin Vacuum-Evaporated Films of Silver	Koreo KINOSITA, Hideki KONDO and Ichiro SAWAMURA	942
Electron Spin Resonance in Irradiated Polytetrafluoroethylene: Decomposition of the Complex Spectrum	Naoyuki TAMURA	943

Errata

Theory of Viscoelasticity of Amorphous Polymers, II. A Note on the Time-Temperature Reducibility of the Relaxation and Retardation Spectra.....	Osamu NAKADA	945
Measures of Finite Strain and Stress-Strain Relations.....	Wataru SEGAWA	945

No. 6

Further Study of the Reaction ${}^7\text{Li}(\gamma, t){}^4\text{He}$	Mitsuo MIWA and Mikio YAMANOUCHI	947
Reactions of Argon-40 with Alpha-Particles.....	Shigeo TANAKA, Michiaki FURUKAWA, Takashi MIKUMO, Shiro IWATA, Masuo YAGI and Hiroshi AMANO	952
On the First and the Second Excited States in Ge^{74}	Toshimitsu YAMAZAKI, Hidetsugu IKEGAMI and Mitsuo SAKAI	957
Theory of Formation Energy of the External and the Internal Surface for Free Electron Metals.....	Akira SUGIYAMA	965
Interaction of Conduction Electrons with Acoustic Waves in Simple Semiconductors	Nobuo MIKOSHIBA	982
Electrical Properties of Germanium Selenide GeSe	Sizuo ASANABE and Atuyosi OKAZAKI	989
Low Field Magnetoresistance Effect of Plastically Deformed n -type Silicon.....	Koji KAMADA	998

Growth and Evaporation of Tungsten Oxide Crystals.....	
.....Hatsujiro HASHIMOTO, Kenzo TANAKA and Eiji YODA	1006
Dislocations in Pure Iron Foils Deformed by Bending	
.....Tadayoshi YAMASHITA and Youji TANEDA	1015
Dynamical Theory of Electron Diffraction in Laue-case, III. Forbidden Reflection	
.....Fuminori FUJIMOTO	1022
Study on the Ordered Alloys of Gold-Manganese System by Electron Diffraction,	
I. Au_3Mn	Denjiro WATANABE 1030
Re-appreciation of the Second Order Transition Phenomena in Polyethylene	
.....Ryuichi NAKANE	1040
The Binding Energy of the σ Bond, I. General Theory.....	Kiyosi O-OHATA 1048
Intramolecular NMR Second Moment of the Polymer Chain.....	Akira MIYAKE 1057
Zeeman Quadrupole Spectra in <i>p</i> -dichlorobenzene and <i>p</i> -chlorobenzoic Acide	
.....Shizuko OGAWA and Kikuo OHI	1064
Statistical Mechanics of Antiferromagnetic Layer Crystal, FeCl_2	Sigeo YOMOSA 1068
Ionization in Argon Mixtures by Electrons in an Electric Field	Mikiya YAMANE 1076
Non-linear Effects on Electron-Plasma Oscillations.....	Masao SUMI 1086
Oscillations in a Plasma in a Weak Magnetic Field.....	Kiyoe KATO 1093
Transport Properties of Plasmas in a Strong Magnetic Field.....	
.....Taro KIHARA, Yukio MIZUNO and Shobu KANEKO	1101
Flow of a Condensing Vapour with Heat Exchange.....	Keishiro NIU 1108
Selbstzündung des <i>n</i> -Hexan-Luft-Gemisches in Stoßwellen	Kunio TERA0 1113

SHORT NOTES

Magnetic Anisotropy of Chalcopyrite	Teruo TERANISHI 1123
Electron Emission Current from Oxide Coated Cathode Subject to High Electric	
Field	Chokichi SHIBATA 1124
Magnetic Hyperfine Structure of the 3,2 Line of Ammonia.....	
.....Koichi SHIMODA and Kunitaka KONDO	1125
Some Observations on the Domain Walls in Thin Films	
.....Yasuo GONDO and Zenya FUNATOGAWA	1126
On the Possibility of Ferromagnetism for an Electron Gas	Masao SHIMIZU 1127
Structure of Giant Resonance in $\text{Al}^{27}(p, \gamma)$ Reaction	Motoharu KIMURA,
Katsufusa SHODA, Naoshi MUTSURO, Tsutomu TOHEI, Kazuo SATO, Kuni-	
shigu KURODA, Katumi KURIYAMA and Tosimitu AKIBA	1128
The Behaviours of Free Radicals Trapped in γ -Irradiated Polyethylene.....	
.....Hisatsugu KASHIWABARA and Kenichi SHINOHARA	1129
Temperature Dependence of Tunnel Diode Characteristics	Yoshitaka FURUKAWA 1130
Paramagnetic Resonance of $\text{Mn}^{++}\text{-F}^-$ Pair in Sodium Chloride ..	Yasaburo YOKOZAWA 1131
Inverse Solution of the Thomas-Fermi Equation.....	Louis GOLD 1132
A Simple Model of Aqueous Solution of Strong Electrolyte.....	Takeshi SATOH 1134
Correction to the Paper "Two-dimensional Flow of an Ideal Gas with Small Electric	
Conductivity past a Thin Profile".....	Takeo SAKURAI 1135
The Magnetic Properties of Mn-Sn-C Alloys	Mitsuru ASANUMA 1136
Conductivity Induced by Injected Electrons in Liquid Dielectrics.....	
.....Pyong-un CHONG, Tomihiko SUGIMOTO and Yoshio INUISHI	1137

Errata

Magnetic Hyperfine Spectrum of H_2CO by a Maser	
.....Hiroshi TAKUMA, Tadao SHIMIZU and Koichi SHIMODA	1139
Angular Dependencies of Efficiencies for Sodium-Iodide Crystals..	Tadayoshi DOKE,
Atsushi NAKAMOTO, Yasukiyo TAKAMI, Manabu HATTORI and Shinji OKANO	1139
Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO	Kazuko MOTIZUKI 1140

AUTHOR INDEX TO VOL. 15, NOS. 1~6

ABE Ryuji: Theoretical Study on the Properties of Coercive Field of BaTiO ₃ Single Crystal	795
AKIBA Tosimitu: [cf. KIMURA, Motoharu (1128)]	
AMANO Hiroshi: [cf. TANAKA Shigeo (545, 952)]	
AMEMIYA Ayao: [cf. OKADA Yoichi (938)]	
AMORÓS J. L.: [cf. ANNAKA Shoichi (356)]	
ANDO Shigenori: General Theory of Electrically Conducting Perfect Gas Flow past a Three-Dimensional Thin Body	157
ANNAKA Shoichi;	
—— and J. L. AMORÓS: On the X-ray Temperature Diffuse Scattering of Anthracene and Stearic Acid. (S.N.).....	356
ARAI Toshihiro: The Study of the Optical Properties of Conducting Tin Oxide Films and their Interpretation in Terms of a Tentative Band Scheme	916
ASADA Tsunesaburo;	
——, H. SAITO, K. OMURA, T. OKU and M. OKA: Annealing of γ -Ray Damage in Germanium	93
ASAMI Masayuki;	
—— and F. TAKANO: Notes on the Theory of Meissner Effect	669
ASANABE Sizuo;	
—— and Atuyosi OKAZAKI: Electrical Properties of Germanium Selenide GeSe	989
ASANUMA Mitsuru: The Magnetic Properties of Mn-Sn-C Alloys. (S.N.).....	1136
AWANE Katsunobu: [cf. OKURA Hiroshi (934)]	
CHIBA Shu: Magnetic Properties of Iron Phosphide Fe ₂ P	581
CHIKAWA Jun-ichi: Multiple-Anode Proportional Counter X-Ray Diffractometer	602
CHIKAZUMI Soshin;	
——, K. SUZUKI and H. IWATA: Studies on the Magnetic Anisotropy Induced by Cold-Rolling of Ferromagnetic Crystal, II. Iron-Aluminum Alloys	250
CHONG, Pyong-un;	
——, T. SUGIMOTO and Y. INUISHI: Conductivity Induced by Injected Electrons in Liquid Dielectrics. (S.N.)	1137
CHŪJŌ Riichiro: [cf. MIYAKE Akira (198)]	
——: NMR Second Moment of a Radical Oscillating in a Periodic Potential. (S.N.).....	201
DODO Taro: Formation of Plasma by Low Energy Iron Injection and Cyclotron Heating	906
DOI Michiyasu: A Possible Mode of Twin in the ϵ -phase of Cu-Sb Alloy	849
DOKE Tadayoshi;	
——, A. NAKAMOTO, Y. TAKAMI, M. HATTORI and S. OKANO: Angular Dependencies of Efficiencies for Sodium-Iodide Crystals. (S.N.)	737
FORSTAT H.;	
——, G. O. TAYLOR and B. R. KING: Heat Capacity of a Single Crystal of MnCl ₂ ·4H ₂ O. (S.N.)	528
FUJIMOTO Fuminori: Dynamical Theory of Electron Diffraction in Laue-case, II. Numerical Calculation of Intensities	859
——: Dynamical Theory of Electron Diffraction in Laue-case, III. Forbidden Reflection	1022
FUJISAKI Haruo;	
—— and Y. TANABE: Crystal Growth of CdS in the Vertical Furnace. (S.N.).....	204
FUJITA Hiroshi: Non-ideality Effects upon the Sedimentation Equilibrium in a Density Gradient	336
FUKUDA Hisao: [cf. TABATA Tatsuo (364)]	
FUKUDA Kuniya;	
——, A. OKUDA and Y. UCHIDA: Optical Bleaching of R-bands in LiF Crystals. (S.N.)	538

- FUKUI Shuji;
 — and S. HAYAKAWA: Microwave Discharge Chamber. (S.N.)..... 531
- FUKUNAGA Kiyoji: [cf. KIKUCHI Seishi (9); NISIMURA Keigo (754)]
- FUNATOGAWA Zenya: [cf. GONDO Yasuo (1126)]
- FURUKAWA Michiaki: [cf. TANAKA Shigeo (545, 952)]
- FURUKAWA Yoshitaka: Photoconductivity in Nickel Doped Germanium. (S.N.)..... 353
 —: Tunneling Probability in Germanium p - n Junctions. (S.N.)..... 730
 —: Temperature Dependence of Tunnel Diodes Characteristics. (S.N.)....1130
- FURUOYA Takashi: [cf. ISHII Zensho (206)]
 — and Y. SASAKI: Dislocations in Si Single Crystals. (S.N.) 205
- GARBER M.: Magnetic Susceptibility of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$. (S.N.) 734
- GOLD Louis: Inverse Solution of the Thomas-Fermi Equation. (S.N.) 1132
- GOMI Yuzi;
 —, Y. ODANI and M. SUGIHARA: Domain Patterns on Thin Films of Per-
 minvar. (S.N) 533
 — and Y. ODANI: Chain Wall in Permalloy Thin Films. (S.N.) 535
- GONDO Yasuo;
 — and Z. FUNATOGAWA: Some Observations on the Domain Walls in Thin
 Films. (S.N.) 1126
- GOTO Mitita: [cf. KUWAHARA Kaizo (359)]
- GOTO Yorio: [cf. MORITA Susumu (361, 550)]
- GOTOH Kanefusa: Magnetohydrodynamic Flow past a Sphere 189
 —: Stokes Flow of an Electrically Conducting Fluid in a Uniform Magne-
 tic Field 696
- HANADA Reiko: [cf. MORITA Susumu (361, 550)]
- HASEDA Taiichiro: Paramagnetic Susceptibility of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and its Deuterated Salts.. 483
- HASHI Tsuneo;
 —, I. TAKAHASHI, M. YAMANO, M. YAMAMOTO, S. SUZUKI and T. MAKITA:
 Maser Oscillation on 6-6 Line of N^{15}H_3 . (S.N.) 532
- HASHIMOTO Hatsujiro;
 —, K. TANAKA and E. YODA: Growth and Evaporation of Oxide Crystals..1006
- HASIKUNI Mitugi: Temperature Dependence of Infrared Absorption Bands of n -Higher
 Alcohols. (S.N.)..... 941
- HATTORI Manabu: [cf. DOKE Tadayoshi (737)]
- HAYAKAWA Satio: [cf. FUKUI Shuji (531)]
- HAYASHI Izuo: [cf. KIKUCHI Seishi (9, 41), NISIMURA Keigo (754)]
- HAYASHI Nisiki: On the Quasi-two-dimensional Laminar Boundary Layer. (S.N.)..... 208
 —: On Similar Solutions of the Steady Quasi-two-dimensional Incompressible
 Laminar Boundary-layer Equations 522
- HIKI Yosio: Internal Friction of Quartz 586
- HIRAI Akira: Temperature Dependence of T_1 of Cl^{35} in Para-dichloro-benzene. (S.N.) .. 201
- HIRAI Masamitsu: [cf. UETA Masayasu (593)]
- HIRAHARA Eiji: [cf. NAYA Rokuroh (360)]
- HIRAKAWA Hiromasa: [cf. KONDO Kunitaka (303)]
- HIROIKE Eiko: Indirect Nuclear Spin-Spin Couplings in Saturated Hydrocarbon Mole-
 cules 270
- HIROIKE Kazuo: Radial Distribution Function of Fluids, III..... 771
- HIROTA Kozo: [cf. KUSUMOTO Hazime (728)]
- HIROTA Shoichi;
 — and T. IMAI: Electron Microscope Study of the Decomposition Process
 of Oxide Coated Cathods 137
 — and T. IMAI: Electron Microscope of the Decomposition Process of
 Oxide Coated Cathods. (Errata) 539
- HIISATAKE Kazuo;
 —, Y. ISHIZAKI, A. ISOYA, T. NAKAMURA, Y. NAKANO, B. SAHEKI, Y. SAJI
 and K. YUASA: The Reaction $\text{Li}^{7}(p, n)\text{Be}^7$, $\text{B}^{11}(p, n)\text{C}^{11}$ and $\text{Al}^{27}(p, n)\text{Si}^{27}$ at
 8 to 14 MeV 741
- HITAKA Saburo: [cf. NONAKA Itaru (365)]

- HONMA Akio: On the Magnetic Susceptibility of FeF_2 456
- HORIE Tadao;
 —, T. NAGURA and M. OTSUKA: Radiative Collisions between Molecular
 and Electron Beams, V. Angular Momentum Distributions of CH Separating
 from Simple Organic Molecules 641
- HOSOKAWA Iwao: A Refinement of the Linearized Transonic Flow Theory 149
- HU Chuin: [cf. ODA Yukiyasu (760)]
- HUSIMI Kazuo: 180° Domain Wall Motions in BaTiO_3 Crystal. (S.N.) 731
- IGARASHI Yoshitaka: [cf. MIZUSHIMA Yoshihiko (729)]
- IDA Shuichi: [cf. SRATORI Kiiti (210)]
- IZIMA Sigeru: [cf. KIKUCHI Makoto (357)]
- IZUKA Takashi: [cf. KIKUCHI Makoto (935)]
- IKEDA Hiroshi: [cf. KIKUCHI Seishi (41)]
- IKEGAMI Hidetsugu: [cf. YAMAZAKI Toshimitsu (957)]
- IMAI Isamu: Electrical Properties of Stannic Oxide Films. (S.N.) 937
- IMAI Nobuhisa: [cf. OHNISHI Tsuyoshi (896)]
- IMAI Tetsuji: [cf. HIROTA Shoichi (137, 539); MIZUSHIMA Yoshihiko (729)]
- INAWASHIRO Sakari: [cf. NOMURA Yûkichi (510)]
- INOUE Morio: [cf. MIZUNO Hiroyuki (211)]
- INUISHI Yoshio: [cf. CHUNG Pyong-un (1137)]
- ISHIBASHI Yoshihiro: [cf. TAKAHASHI Hidetosi (853)]
- ISHIDA Yôichi: [cf. TANAKA Tomoyasu (261)]
- ISHII Chikai;
 — and K. TAKAHASHI: A Gamma Ray in Ti^{45} Decay. (S.N.) 736
- ISHII Zensho;
 —, T. FURUOYA, Y. SASAKI and K. KOHRA: Observation of Layer Struc-
 ture in Dislocation Free Silicon Crystals with the Use of X-ray Anomalous
 Transmission. (S.N.) 206
- ISHIZAKI Yoshihide: [cf. HISATAKE Kazuo (741)]
- ISOYA Akira: [cf. KIKUCHI Seishi (41); HISATAKE Kazuo (741)]
- ITO Satoru: [cf. KIKUCHI Seishi (41)]
- ITO Takao: [cf. OKADA Yôichi (938)]
- ITOH Junkichi: [cf. KUSUMOTO Hazime (728)]
- IWATA Hiroko: [cf. CHIKAZUMI Sôshin (250)]
- IWATA Shiro: [cf. TANAKA Shigeo (545, 952)]
- KAIFU Yôzo: [cf. TOMURA Masao (314)]
- KAKUTANI Tsunehiko: Axially Symmetric Stagnation-point Flow of an Electrically
 Conducting Fluid under Transverse Magnetic Field 688
- KAMADA Koji: Low Field Magnetoresistance Effect of Plastically Deformed n-type
 Silicon 998
- KANAI Yasuo: The Change in Electron Mobility in Indium Antimonide at Low Electric
 Field 830
- KANEKO Takejiro: Volume Magnetostriction of Cobalt-Nickel Alloys 463
 —: Volume Magnetostriction of Cobalt-Nickel Alloys. (Errata) 738
- KANZAKI Hiroshi;
 — and K. KIDO: Purification of Alkali Halide Crystals through Fractional
 Distillation and Normal Freezing. (S.N.) 529
- KARASAWA Takashi: [cf. KIKUCHI Seishi (41)]
- KASHIWABARA Hisatsugu;
 — and K. SHINOHARA: The Behaviors of Free Radicals Trapped in γ -Ir-
 radiated Polyethylene. (S.N.) 1129
- KASUYA Takahiro;
 — and T. OKA: Microwave Spectrum of Ethyl Iodide, I 296
- KATO Kiyoe: Oscillations in a Plasma in a Weak Magnetic Field 1093
- KATO Yoshinori: [cf. NISHIOKA Atsuo (416)]
- KAUFFMAN J. W.: [cf. NENNO Soji (220)]
- KAWAI Nawoyuki: [cf. MORITA Susumu (361, 550)]
 —: On the Alpha-particles from the $\text{N}^{14}(d, \alpha)\text{C}^{12}$ Ground State Reaction.

- (S.N.)..... 930
- KAWAJI Shinji: A.C. and D.C. Field Effects on Cleaned Germanium Surfaces 95
- KAWAMURA Mitsuhiro: Angular Correlation Measurements in the Decay of $\text{In}^{114\text{m}}$ 3
- KIDO Keishiro: [cf. KANZAKI Hiroshi (529)]
- KIHARA Taro;
 —, Y. MIDZUNO, K. SAKUMA and T. SHIZUME: Ion-Electron Relaxation of
 Plasmas in a Magnetic Field, II..... 684
 —, Y. MIDZUNO and S. KANEKO: Transport Properties of Plasmas in a
 Strong Magnetic Field 1101
- KIKUCHI Ken: [cf. KIKUCHI Seishi (41); ODA Yukiyasu (760)]
- KIKUCHI Makoto;
 — and S. IIZIMA: Photoconductivity of Cd-ZnS Mixed Crystals. (S.N.).... 357
 — and K. TACHIKAWA: Visible Light Emission and Microplasma Pheno-
 mena in Silicon $p-n$ Junction, I 835
 — and T. IIZUKA: Observation of Microplasma Pulses and Electrolumines-
 cence in Gallium Phosphide Single Crystal. (S.N.) 935
- KIKUCHI Seishi;
 —, J. SANADA, S. SUWA, I. HAYASHI, K. NISIMURA and K. FUKUNAGA:
 Elastic Scattering of 14 Mev Protons by Deuterons and by Protons..... 9
 —, I. NONAKA, H. IKEDA, H. KUMAGAI, Y. SAJI, J. SANADA, S. SUWA, A.
 ISOYA, I. HAYASHI, K. MATSUDA, H. YAMAGUCHI, T. MIKUMO, K. NISIMURA,
 T. KARASAWA, S. KOBAYASHI, K. KIKUCHI, S. ITO, A. SUZUKI, S. TAKEUCHI
 and H. OGAWA: A 160 cm Synchro- and Variable Energy Ordinary Cyclotron.. 41
 —, et al.: A 160 cm Synchro- and Variable Energy Ordinary Cyclotron.
 (Errata)..... 527
 —, J. SANADA, S. SUWA, I. HAYASHI, K. NISIMURA and K. FUKUNAGA:
 Protons from the $p+d$ Breakup Reaction at Proton Energies of 14 MeV and
 10 MeV 749
- KIM Pil Hyon: On the Proton Resonance of Several Hexammine Complex Salts 445
- KIMURA Motoharu;
 —, K. KURIYAMA, K. SHODA, N. MUTSURO, T. TOHEI, T. AKIBA, K. SATO
 and K. KURODA: Structure of Giant Resonance in $\text{Al}^{27}(p, \gamma)$ Reaction. (S.N.)..1128
- KING B. R.: [cf. FORSTAT, H. (528)]
- KINOSITA Koreo;
 —, H. KONDO and I. SAWAMURA: Stress in Very Thin Vacuum-Evaporated
 Films of Silver. (S.N.) 942
- KOBAYASHI Shinsaku: [cf. KIKUCHI Seishi (41); ODA Yukiyasu (760)]
- KOHRA Kazutake: [cf. ISHII Zensho (206)]
- KOIKE Yasuhiro: [cf. NISHIOKA Atsuo (416)]
- KOJIMA Shoji;
 — and M. MINEMATSU: Nuclear Quadrupole Resonance of Nitrogen in
 Cyanuryl Chloride. (S.N.) 355
- KOJIMA Takeshi: Potential Barrier of Phenol from its Microwave Spectrum 284
- KOMATSUBARA Kiichi: [cf. KURATA Takao (362)]
- KONDO Hideki: [cf. KINOSITA Koreo (942)]
- KONDO Kunitaka: [cf. SHIMODA Koichi (1125)]
 —, H. HIRAKAWA, A. MIYAHARA, T. OKA and K. SHIMODA: Microwave
 Zeeman Effect of Formaldehyde 303
 — and T. OKA: Stark-Zeeman Effects on Asymmetric Top Molecules. For-
 maldehyde H_2CO 307
- KONDOH Hisamoto: [cf. UCHIDA Enji (466)]
- KONO Ryusuke: The Dynamic Bulk Viscosity of Polystyrene and Polymethyl Metha-
 crylate 718
- KONO Tatsuo: [cf. TAKAHASHI Minoru (936)]
- KRISHNAMURTHI M.;
 — and M. SURYANARAYANA: Ultrasonic Propagation through Aqueous So-
 lutions of Acetates 345
 — and M. SURYANARAYANA: Ultrasonic Propagation through Binary Mix-

- tures containing Acetic Acid 349
- KUBO Hiroshi: [cf. MITANI Kenji (678)]
- KUMAGAI Hiroo: [cf. KIKUCHI Seishi (41)]
- KURATA Takao;
 ——— and K. KOMATSUBARA: A Curious Characteristic of P-N-P-N Junctions.
 (S.N.)..... 362
- KURIYAMA Katumi: [cf. KIMURA Motoharu (1128)]
- KURODA Kunishige: [cf. KIMURA Motoharu (1128)]
- KUROSAWA Tatumi: [cf. YAMASHITA Jiro (802)]
- KUROYANAGI Tokihiro: [cf. MORINAGA Haruhiko (213)]
- KUSUMOTO Hazime;
 ———, J. ITOH, K. HIROTA and T. UEDA: On the Proton Chemical Shift in
 Deuterium Substituted *p*-Xylene and Toluene. (S.N.)..... 728
- : The Effects of Deuteron Irradiation on the Nuclear Magnetic Resonance in Teflon 867
- KUWAHARA Kaizo;
 ——— and Mitita GOTO: Thickness Dependence of Domain Orientation in Thin
 Nickel Films. (S.N.) 359
- MAKITA Tsutomu: [cf. TAKAHASHI Isao (532)]
- MATSUDA Kazuhisa: [cf. KIKUCHI Seishi (41); ODA Yukiyasu (760)]
- MATSUMURA Tetsuo;
 ——— and Y. TANABE: Synthesis of AlN Crystals. (S.N.) 203
- MATSUZAWA Kiichiro: Condenser Microphones with Plastic Diaphragms for Airborne
 Ultrasonics, II 167
- MCIRVINE E. C.: Screened Impurity Potentials in Metals. (S.N.) 928
- MELKONIAN Edward: [cf. WAJIMA John T. (630)]
- MIDZUNO Yukio: [cf. KIHARA Taro (684, 1101)]
- MIKOSHIBA Nobuo: Interaction of Conduction Electrons with Acoustic Waves in Simple
 Semiconductors 982
- MIKUMO Takashi: [cf. KIKUCHI Seishi (41); TANAKA Shigeo (545, 952); NONAKA Itaru
 (365)]
- MINEMATSU Midori: [cf. KOJIMA Shoji (355)]
- MISHINA Masanori: [cf. MUTSURO Naoshi (358)]
- MITANI Kenji;
 ——— and H. KUBO: Breakdown of Argon at Low Pressure in a Longitudinal
 Magnetic Field 678
- MITSUI Hidehiko: [cf. MORINAGA Haruhiko (213)]
- MITSUI Tadayasu: [cf. SATŌ Masayoshi (537)]
 ———: Magnetic Anisotropy Induced by Cold Rolling of Cu-Co Alloy. (S.N.).. 929
- MIWA Mitsuo;
 ——— and M. YAMANOUCHI: Further Study of the Reaction ${}^7\text{Li}(\gamma, t){}^4\text{He}$ 947
- MIYADAI Tomonao: [cf. SHICHIJŌ Yūzō (530)]
- MIYAHARA Akira: [cf. KONDO Kunitaka (303)]
- MIYAKE Arira;
 ——— and R. CHŪJŌ: Influence of Foreign Magnetic Nuclei on NMR. (S.N.).. 198
- : On the Intramolecular Light Scattering of the Non-Gaussian Chain .. 875
- : Influence of the Molecular Weight Distribution on the Polymer Properties 883
- : Intramolecular NMR Second Moment of the Polymer Chain.....1057
- MIYAMOTO Shigeo: [cf. OHKURA Hiroshi (934)]
- MIZUNO Hiroyuki;
 ——— and M. INOUE: Formation Mechanism of F-Centers in KCl Single Crystals Heated in Potassium Vapor 211
- MIZUSHIMA Sanchi: Dislocation Model of Liquid Structure 70
- MIZUSHIMA Yoshihiko;
 ———, Y. IGARASHI and T. IMAI: Cold-emitting Cathode Materials. (S.N.)... 729
- MIZUTANI Hiroshi: Effect of Solvent on the Extension of High Polymer Molecule.... 475
- MORINAGA Haruhiko;

- , T. KUROYANAGI, H. MITSUI and K. SHODA: Three New Isotopes, Co^{63} , Ga^{75} and As^{81} 213
- MORINO Yonezo;
 ——— and M. TOYAMA: Zeeman Effect of Nuclear Quadrupole Resonance Spectrum in 1, 3, 5-Trichlorobenzene 288
- MORITA Susumu;
 ———, N. KAWAI, N. TAKANO, Y. GOTO, R. HANADA, Y. NAKAJIMA, S. TAKE-MOTO and Y. YAEGASHI: Differential Cross Sections for the $\text{N}^{14}(d, p)\text{N}^{15}$ Ground State Reaction at the Deuteron Energy of 16 MeV..... 361
 ———, N. KAWAI, N. TAKANO, Y. GOTO, R. HANADA, Y. NAKAJIMA, S. TAKE-MOTO and Y. YAEGASHI: Differential Cross Sections for the Reaction $\text{C}^{12}(d, p)\text{C}^{13}$ in the Energy Range of Deuterons from 15- to 20-MeV..... 550
- MOTIZUKI Kazuko: Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO 888
 ———: Theory of the Nuclear Magnetic Resonance of Co^{59} in CoO . (Errata)..1140
- MURAKAMI Miyuki: [cf. NAYA Rokuroh (300)]
- MURAKAMI Terutosi: On the Variation Principle in the Kinetic Theory of Dense Gases, I 60
- MUTO Jiro: Investigation of the Reaction $\text{Mg}^{25}(p, \gamma)\text{Al}^{26}$ 17
- MUTSURO Naoshi: [cf. KIMURA Motoharu (1128)]
 ———, K. SATO and M. MISHINA: Fine Structure in the $\text{N}^{14}(\gamma, n)\text{N}^{13}$ Activation Curve, II. (S.N.) 358
- NAGAHARA Yukio: [cf. ODA Yukiyasu (760)]
- NAGAI Kazuo: Configurational Changes of Polypeptide Molecules in the Helix-Coil Transition Region, I 407
- NAGAMIYA Takeo: [cf. UCHIDA Enji (466)]
- NAGAO Shigeo;
 ——— and Teruyuki SATO: Some Experiments on Plasma Alfvén Waves. (S.N.)..... 375
- NAGATANI Kunio: Radiations from Ba^{141} 1
- NAGURA Takayuki: [cf. HORIE Tadao (641)]
- NAKADA Osamu: Theory of Viscoelasticity of Amorphous Polymers, II. A Note on the Time-Temperature Reducibility of the Relaxation and Retardation Spectra (Errata) 945
- NAKAGAWA Yasuaki: [cf. TEZUKA Seiji (931)]
- MAKAJIMA Yutaka: [cf. MORITA Susumu (361, 550)]
- NAKAMOTO Atsushi: [cf. DOKE Tadayoshi (737)]
- NAKAMURA Teruo: [cf. HISATAKE Kazuo (741)]
- NAKAMURA Terutaro: [cf. TAKAHASHI Hidetosi (853)]
- NAKANE Ryuichi: Re-appreciation of the Second Order Transition Phenomena in Polyethylene 1040
- NAKANO Yoshihiro: [cf. HISATAKE Kazuo (741)]
- NAKAU Tanehiro: Electrical Conductivity of $\alpha\text{-Fe}_2\text{O}_3$. (S.N.) 727
- NAKAZUMI Yoshihide: [cf. UCHIDA Enji (466)]
- NARABA Tsunezo: [cf. NISHIOKA Atsuo (416)]
- NARITA Shin-ichiro: Electroluminescence in Zinc Sulfide Single Crystals..... 128
- NAYA Rokuroh;
 ———, M. MURAKAMI and E. HIRAHARA: Magnetic and Electrical Anomalies of Iron Telluride Single Crystals 360
- NEGISHI Katsuo: Jump Phenomenon in Resonance Curve of Ferroelectric Ceramics. (S.N.)..... 534
- NENNO Soji;
 ——— and J. W. KAUFFMAN: Detection and Determination of Equilibrium Vacancy Concentrations in Aluminum 220
- NIMURA Hiroshi: Crystal Texture of LiF Single Crystal by X-Ray Technique 231
- NISHIKAWA Kyoji: Approach to Equilibrium of A Large Fermion System 78
- NISHIMURA Jiro: The Dislocation Etch Pits of CdS Crystals. (S.N.) 732
- NISHIOKA Atsuo;
 ———, Y. KOIKE M. OWAKI, T. NARABA and Y. KATO: Proton Magnetic

- Resonance and X-ray Diffraction Studies of Polypropylene 416
- NISIMURA Keigo; [cf. KIKUCHI Seishi (9, 41)]
- , S. SUWA, I. HAYASHI, K. FUKUNAGA, N. RYU and M. SEKI: Measurements of the Polarization in Proton-Helium Elastic Scattering 754
- NIU Keishiro: Flow of a Condensing Vapor with Heat Exchange 1108
- NOMURA Yûkichi;
- , I. YAMAMURA and S. INAWASHIRO: On the Acoustic Radiation from a Flanged Circular Pipe 510
- NONAKA Itaru; [cf. KIKUCHI Seishi (41)]
- , H. YAMAGUCHI, T. MIKUMO, I. UMEDA, T. TABATA and S. HITAKA: Angular Distributions of Protons from the Reactions $^{12}\text{C}(\alpha, p)^{13}\text{N}$. (Errata).. 365
- ODA Yukiyasu;
- , M. TAKEDA, T. YAMAZAKI, C. HU, N. TAKANO, K. KIKUCHI, S. KOBAYASHI, K. MATSUDA and Y. NAGAHARA: Elastic and Inelastic Scattering of Protons from N, Ne, Mg, Si, S and A in the Energy Range from 7.6 MeV to 14.2 MeV 760
- ODANI Yuza; [cf. GOMI Yuzi (533, 535)]
- OGAWA Hiroshi; [cf. KIKUCHI Seishi (41)]
- OGAWA Sekiko;
- and Syoten OKA: Theory of Electric Birefringence in Dilute Solutions of Tobacco Mosaic Virus 658
- OGAWA Shizuko;
- and K. OHI: Zeeman Quadrupole Spectra in p-dichlorobenzene and p-chlorobenzoic Acid 1064
- OHI Kikuo; [cf. OGAWA Shizuko (1064)]
- OHKURA Hiroshi;
- , K. AWANE and S. MIYAMOTO: On the $F \rightarrow F'$ Conversion in the Presence of A-, M-, R-, and Z_1 -Centers. (S.N.) 934
- OHNISHI, Tsuyoshi;
- , N. IMAI and F. OOSAWA: Interaction between Rod-like Polyelectrolytes.. 896
- OHTA Tokio: Effect of Charged Dislocation on the Thermoelectric Power of Semiconductors. (S.N.) 197
- OHTSUKA Taiichiro: Interaction Effects in $\text{K}_3\text{Fe}(\text{CN})_6$. (S.N.) 939
- OKA Masahiro; [cf. ASADA Tsunesaburo (93)]
- OKA Syoten; [cf. OGAWA Sekiko (658)]
- OKA Takeshi; [cf. KASUYA Takahiro (296); KONDO Kunitaka (303, 307)]
- OKADA Kenkichi: Some Properties of X-ray damaged Rochelle Salt. (S.N.) 363
- OKADA Yôichi;
- , T. ITO and A. AMEMIYA: Post-Irradiation Effect in Visible Absorption Spectra of Polyvinyl Chloride Sheets. (S.N.) 938
- OKAMOTO Hiroshi: Theory of Solutions of Chain Molecules 650
- OKANO Kotoyuki; [cf. TABATA Tatsuo (364)]
- : Gamma-rays from the Reaction $\text{Al}^{27}(p\gamma)\text{Si}^{28}$ 28
- OKANO Masaharu; [cf. DOKE Tadayoshi (737)]
- OKAZAKI Atuyosi; [cf. ASANABE Sizuo (989)]
- OKU Taiji; [cf. ASADA Tsunesaburo (93)]
- OKUDA Akizo; [cf. FUKUDA Kuniya (538)]
- OMORI Yoshirô: An Investigation of Psychrometer, II. 706
- OMURA Kazumi; [cf. ASADA Tsunesaburo (93)]
- O-OHATA Kiyosi: The Binding Energy of the σ Bond, I. General Theory..... 1048
- OOSAWA Fumio; [cf. OHNISHI Tsuyoshi (896)]
- OSADA Kikusaburo: Thermoluminescence of Zinc Sulfide Phosphors 145
- OTSUKA Masamoto; [cf. HORIE Tadao (641)]
- OWAKI Masakazu; [cf. NISHIOKA Atsuo (416)]
- RUSTAD Brice; [cf. WAJIMA John. T. (630)]
- RYU Norio; [cf. NISIMURA Keigo (754)]
- SABURI Osamu: Piezoresistivity in Semiconductive Barium Titanates. (S.N.)..... 733
- SAHEKI Bunsaburo; [cf. HISATAKE KAZUO (741)]

- SAITO Haruo: [cf. ASADA Tsunesaburo (93)]
- SAJI Yoshio: [cf. KIKUCHI Seishi (41); HISATAKE Kazuo (741)]
- : Energy Spectrum and Angular Distributions of Neutrons from the Reaction $\text{Be}^9(p, n)\text{B}^9$ at 8 to 14 MeV of Proton Energies 367
- SAKAI Mitsuo: [cf. YAMAZAKI Toshimitsu (957)]
- : Spin Order in the Doublet at the Second Excited Level in Even-even Medium Nuclei. (S.N.) 993
- SAKAI Sukeyoshi: [cf. TEZUKA Seiji (931)]
- SAKUMA Kyoko: [cf. KIHARA Taro (684)]
- SAKURAI Takeo: Two-dimensional Flow of an Ideal Gas with Small Electric Conductivity past a Thin Profile 326
- : Correction to the Paper "Two-dimensional Flow of an Ideal Gas with Small Electric Conductivity past a Thin Profile". (S.N.) 1135
- SANADA Junpei: [cf. KIKUCHI Seishi (9, 41)]
- SASAKI Wataru: [cf. SHIBUYA Motoichi (207)]
- SASAKI Yozo: [cf. FURUOYA Takashi (205); ISHII Zensho (206)]
- SATO Kazuo: [cf. KIMURA Motoharu (1128); MUTSURO Naoshi (358)]
- SATŌ Masayoshi:
- and T. MITUI: Influence of Preparation and Quenching on the Magnetic Properties of Precipitates in Cu-Co Alloy. (S.N.) 537
- SATO Teruyuki: [cf. NAGAO Shigeo (735)]
- SATOH Takeshi: A Simple Model of Aqueous Solution of Strong Electrolyte. (S.N.) .. 1134
- SAWADA Shozo: [cf. YOSHIDA Ikushi (199)]
- SAWAMURA Ichiro: [cf. KINOSITA Koreo (942)]
- SEGAWA Wataru: Maxwell's Formula for Three-Dimensional and Large Deformation.. 339
- : Measures of Finite Strain and Stress-Strain Relations..... 518
- : Maxwell's Formula for Three-Dimensional and Large Deformation (Errata)..... 738
- : Measures of Finite Strain and Stress-Strain Relations (Errata) .. 945
- SEKI Masao: [cf. NISIMURA Keigo (754)]
- SHIBATA Chokichiro: Electron Emission Current from Oxide Coated Cathode Subject to High Electric Field. (S.N.) 200
- SHIBATA Noboru: On a Solution of the Paraxial Ray Equation in an Axially Symmetrical Electrostatic Field. (S.N.) 200
- SHIBUYA Motoichi;
- and W. SASAKI: Intervalley Scattering of Hot Electrons. (S.N.) 207
- SHIICHIRŌ YŪzō;
- , T. MIYADAI and H. TAKATA: Ferrimagnetic Resonance in Polycrystalline Europium-Iron Garnet ($\text{Eu}_3\text{Fe}_5\text{O}_{12}$). (S.N.) 530
- SHIMADA Akira: [cf. TOYODA Koichi (536)]
- SHIMAOKA Kohji: Electron Diffraction Study of Ice 106
- SHIMIZU Masao: On the Stability of an Electron Gas at Low Density 217
- : Ferromagnetism of an Electron Gas 376
- : On the Possibility of Ferromagnetism for Electron Gas. (S.N.) 1127
- SHIMIZU Tadao;
- and H. TAKUMA: Microwave Spectrum of Cis-1, 2-Dichloroethylene .. 646
- SHIMODA Koichi: [cf. KONDO Kunitaka (303)]
- and K. KONDO: Magnetic Hyperfine Structure of the 3, 2 Line of Ammonia. (S.N.) 1125
- SHINOHARA Kenichi: [cf. KASHIWABARA Hisatsugu (1129)]
- SHIRAIWA Toshio: The Theory of the Fine Structure of the X-ray Absorption Spectrum, II. 240
- SHIZUME Toshio: [cf. KIHARA Taro (684)]
- SHODA Katsufusa: [cf. MORINAGA Haruhiko (213); KIMURA Motoharu (1128)]
- SIRATORI Kiiti;
- and S. IIDA: Magnetic Properties of $\text{Mn}_x\text{Cr}_{1-x}\text{O}_2$. (S.N.) 210
- SŌMA Shinzan;
- and Y. TAKEUCHI: A New Type of Thermal Conductivity Gas Detector, I. 333

- SUGIHARA Makoto: [cf. GOMI Yuzi (533)]
- SUGIMOTO Tomihiko: [cf. CHONG Pyong-un (1137)]
- SUGIYAMA Akira: Theory of Formation Energy of the External and the Internal Surface for Free Electron Metals 965
- SUMI Masao: Theory of Electron-Oscillations in Non-Uniform Plasmas 120
- : Non-Linear Effects on Electron-Plasma Oscillations 1086
- SURYANARAYANA M.: [cf. KRISHNAMURTHI M. (345, 349)]
- SUWA Shigeki: [cf. KIKUCHI Seishi (9, 41); NISIMURA Keigo (754)]
- SUZUKI Arata: [cf. KIKUCHI Seishi (41)]
- SUZUKI Kenzō: [cf. CHIKAZUMI Sōshin (250)]
- SUZUKI Shigeyoshi: [cf. TAKAHASHI Isao (532)]
- TABATA Tatsuo;
- , H. FUKUDA and K. OKANO: Lower Excited States in P^{29} . (S.N.) 364
- TABATA Tetsuo: [cf. NONAKA Itaru (365)]
- TACHIKAWA Kenkichi: [cf. KIKUCHI Makoto (835)]
- TAKAHASHI Isao;
- , T. HASHI M. YAMANO, M. YAMAMOTO S. SUZUKI and T. MAKITA: Maser Oscillation on 6-6 Line of $N^{16}H_3$. (S.N.) 532
- TAKAHASHI Kasuke: [cf. ISHII Chikai (736)]
- TAKAHASHI Minoru;
- and T. KōNO: Magnetic Annealing of Co and Co-Ni Alloys. (S.N.).... 936
- TAKAHASHI Hidetosi;
- , T. NAKAMURA and Y. ISHIBASHI: Shape of Nucleus Domain Anchored to a Screw Dislocation in Ferroelectric Crystal 853
- TAKAMI Yasukiyo: [cf. DOKE Tadayoshi (737)]
- TAKANO Fumihiko: [cf. ASAMI Masayuki (669)]
- TAKANO Naoyuki: [cf. MORITA Susumu (361, 550); ODA Yukiyasu (760)]
- TAKATA Hisao: [cf. SHICHIJō Yūzō (530)]
- TAKEDA Minoru: [cf. ODA Yukiyasu (760)]
- : Elastic and Inelastic Scattering of 11.2 MeV Deuterons 557
- TAKEMOTO Shigeo: [cf. MORITA Susumu (361, 550)]
- TAKEUCHI Seiichiro: [cf. KIKUCHI Seishi (41)]
- TAKEUCHI Yū: [cf. SōMA Shinzan (33)]
- TAKUMA Hiroshi: [cf. SHIMIZU Tadao (646)]
- TAMURA Naoyuki: Electron Spin Resonance in Irradiated Polytetrafluoroethylene: Decomposition of the Complex Spectrum. (S.N.) 943
- TANABE Yasaku: [cf. MATSUMURA Tetsuo (203); FUJISAKI Haruo. (204)]
- TANAKA Kenzo: [cf. HASHIMOTO Hatsujiro (1006)]
- TANAKA Shigeo;
- , M. FURUKAWA, T. MIKUMO, S. IWATA, M. YAGI and H. AMANO: Excitation Functions for Alpha-Induced Reactions on Manganese-55 545
- , M. FURUKAWA, T. MIKUMO, S. IWATA, M. YAGI, and H. AMANO: Reactions of Argon-40 with Alpha-Particles 952
- TANAKA Shoji: [cf. TANAKA Toshio (726)]
- TANAKA Tetsuro: [cf. TOYODA Koichi (536)]
- TANAKA Tomoyasu;
- and Y. ISHIDA: Dielectric Relaxation in High Polymers, II. Vinylic High Polymers 261
- TANAKA Toshio;
- , and S. TANAKA: Measurement of Piezoelectric Constants of a CdS Crystal. (S.N.) 726
- TANEDA Youji: [cf. YAMASHITA Tatsumi (1015)]
- TANISAKI Sigetosi: On the Phase Transition of Tungsten Trioxide below Room Temperature 566
- : Crystal Structure of Monoclinic Tungsten Trioxide at Room Temperature 573
- TAYLOR G. O.: [cf. FORSTAT H. (528)]
- TERANISHI Teruo: Magnetic Anisotropy of Chalcopyrite. (S.N.) 1023

TERAO Kunio: Selbstzündung des n-Hexan-Luft-Gemisches in Stoßwellen	1113
TERAO Nobuzo: Une Nouvelle Forme du Nitrure de Nickel: Ni_4N	227
TEZUKA Seiji;	
———, S. SAKAI and Y. NAKAGAWA: Ferromagnetism of Mn-Zn Alloy. (S.N.)	931
TIERS George Van Dyke: Fluorine N.S.R. Spectroscopy, II. A "Distant" Carbon-13 Isotope Effect. (S.N.)	354
TŌHEI Tsutomu: [cf. KIMURA Motoharu (1128)]	
———: Decay of Cl^{34m}	372
TOMIKO Tetsuhiko: Photo- and Thermochemical Reactions in Potassium Chloride Crystals—A Quantitative Study of the M Centre	488
TOMITA Takanori: Crystal Structure of Silicon Carbide of 174 Layers	99
TOMURA Masao;	
——— and Y. KAIFU: Luminescences from KBr/KI Single Crystals	314
TOYAMA Masaharu: [cf. MORINO Yonezo (288)]	
———: Relative Intensities of Zeeman Components in Nuclear Quadrupole Resonance Spectrum. (Errata)	196
TOYODA Koichi;	
———, A. SHIMADA and T. TANAKA: Diffuse Scattering of X-ray by Gamma-ray Irradiated Rochelle Salt	536
UCHIDA Enji;	
———, H. KONDOH, Y. NAKAZUMI and T. NAGAMIYA: Magnetic Anisotropy Measurements of MnO Single Crystal	466
UCHIDA Yoichi: [cf. FUKUDA Kuniya (538)]	
UEDA Tomiko: [cf. KUSUMOTO Hazime (728)]	
UEHARA Yasuo: The Quantitative Interpretation of Luminescent Properties of Cu- Activated Calcium Orthophosphate	612
UETA Masayasu;	
———, M. HIRAI and H. WATANABE: Interaction of Exciton with Electron Trapping Centers in Alkali Halide Crystals, 2. Quantum Yield for the $U \rightarrow F'$ Conversion and its Dependence on U -Center Concentration	593
UMEDA Iwao: [cf. NONAKA Itaru (365)]	
WAJIMA John T.;	
———, B. M. RUSTAD and E. MELKONIAN: Germanium Crystal as a Neutron Monochrometer and the Determination of its Higher Order Contaminations..	630
WATANABE Denjiro: Study on the Ordered Alloys of Gold-Manganese System by Elec- tron Diffraction, I. Au_3Mn	989
WATANABE Hiroyuki: [cf. UETA Masayasu (593)]	
YAEHASHI Yûki: [cf. MORITA Susumu (361, 550)]	
YAGI Masuo: [cf. TANAKA Shigeo (545)]	
YAMADA Yasusada: On the Paramagnetic Inelastic Scattering of Neutrons due to Ions in the Anisotropic Crystalline Field	429
YAMAGUCHI Hisashi: [cf. KIKUCHI Seishi (41)]	
YAMAMOTO Motokazu: [cf. TAKAHASHI Isao (532)]	
YAMAMURA Ichirô: [cf. NOMURA Yûkichi (510)]	
YAMANE Mikiya: Ionization in Argon Mixtures by Electrons in an Electric Field	1076
YAMANO Masaru: [cf. TAKAHASHI Isao (532)]	
YAMANOUCHI Mikio: [cf. MIWA Mitsuo (947)]	
YAMASHITA Jiro;	
——— and T. KUROSAWA: Heitler-London Approach to Electrical Conductivity and Application to d -Electron Conductions	802
YAMASHITA Tadayoshi;	
——— and Y. TANEDA: Dislocations in Pure Iron Foils Deformed by Bending..	1015
YAMAZAKI Takashi: [cf. ODA Yukiyasu (760)]	
YAMAZAKI Toshimitsu;	
———, H. IKEGAMI and M. SAKAI: On the First and the Second Excited States in Ge^{74}	957
YASUHARA Michiru: Flow of a Viscous, Electrically Conducting Fluid along a Circular Cylinder or a Flat Plate with Uniform Suction	321

- YASUKŌCHI Kō;
 ———, K. KANEMATSU and T. OHYAMA: Ferrimagnetism of Mn_3Ge_2 . (S.N.).. 932
 YODA Eiji: [cf. HASHIMOTO Hatsujiro (1006)]
 ———: Anomalous Growth of MoO_3 Crystals..... 821
 YOKOTA Toshio: Expansion Theorem of Density Matrix, Virial Expansion and New
 Formula of Multiple Scattering 779
 YOKOZAWA Yasaburo: Paramagnetic Resonance of $\text{Mn}^{++}\text{-F}^-$ Pair in Sodium Chloride.
 (S.N.).....1131
 YOMOSA Sigeo: Statistical Mechanics of Antiferromagnetic Layer Crystal, FeCl_2 1068
 YOSHIDA Ikushi;
 ——— and S. SAWADA: Thermal Conductivity of KNO_3 . (S.N.) 199
 YOSHIMURA Hisamitsu: Paramagnetic Resonance of Manganese in Alkali-Chlorides.... 435
 YOSINOBU Hirowo: A Linearized Theory of Magnetohydrodynamic Flow past a Fixed
 Body in a Parallel Magnetic Field..... 175
 YUASA Kazunori: [cf. HISATAKE Kazuo (741)]

80792

RES. AUG 30 '76

JUL 20 16 '79

SCI. LIB

MAY 20 1981

GAYLORD

PRINTED IN U. S. A.

GAYLORD

PRINTED IN U.S.A.

3 8198 314 284 165

